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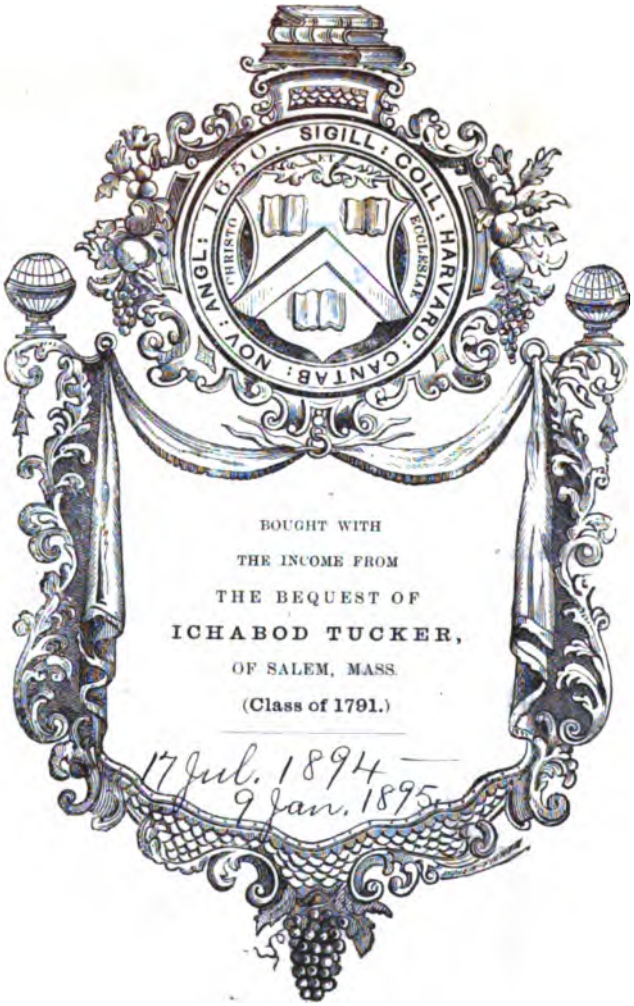

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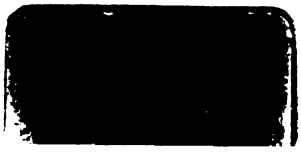

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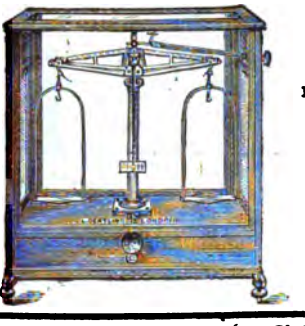

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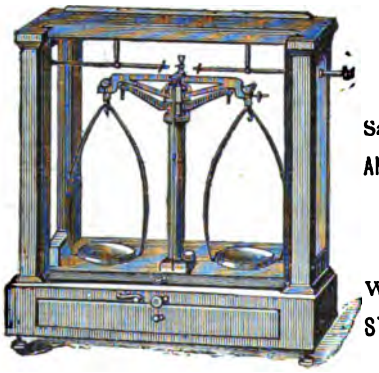

FIG. 3*a*.

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VOLUME LXX.

EDITED BY WILLIAM CROOKES, F.R.S., &c.

No. 1806.—JULY 6, 1894.

ON SOME

ANALYTICAL CONSTANTS OF SEAL OIL.

By ALFRED C. CHAPMAN, F.I.C., and J. F. ROLFE.

One of the authors of this paper having had on several occasions to examine samples of seal oil with a view to detecting possible adulteration with other animal and vegetable oils, it was thought advisable to carefully examine several genuine samples in order to obtain a number of analytical constants for this oil, such as are required in the analytical examination of natural fixed oils. Most of these constants had been determined by previous observers, but since one or two of the numbers have not been to our knowledge before recorded, and as two of our determinations differ from those of other workers, we have thought that our results might be of interest and possibly of use to chemists engaged in the examination of oils.

In addition we have given in the Table below the results obtained on applying the same analytical methods to a sample of "blown" seal oil, which has not, so far as we know, been before examined.

Six samples of oil of different qualities were examined. All of these samples were obtained through the courtesy of large wholesale oil merchants, and of their genuineness there can be little or no doubt.

Remarks upon the Above Numbers.

Specific Gravity.—The specific gravity of these samples was taken in a specific gravity bottle at 15° C. (water at 15° C. = 1). It will be seen that our results, which agree with the published numbers of other experimenters, vary very slightly in the case of the first five samples. The specific gravity of the "brown seal oil" is somewhat lower, as is very frequently observed in the case of oils containing a considerable percentage of free fatty acids. Thomson and Ballantyne (*Journ. Soc. Chem. Ind.*, 1890, p. 588) have shown, however, that this is not always the case.

Melting-point of the Insoluble Fatty Acids.—This was determined in capillary tubes open at both ends, the level of the water in the bath being somewhat above that of the fat in the tubes. The temperature at which the fat commenced to ascend the tubes was taken as the melting-point.

Iodine Absorption.—In these determinations we made use of Hübl's solution. A considerable excess of this solution was added to a solution of a weighed quantity of the oil in chloroform. After allowing the mixture to stand for five hours the excess of iodine was determined by titrating with a standardised solution of sodium thiosulphate.

In all these experiments the excess of iodine was approximately equal to the amount with which the oil united.

The only recent iodine-absorption numbers for seal oil of which we know are those published by Thomson and Ballantyne in their valuable paper above referred to. Our numbers agree on the whole with those recorded by these chemists. The time allowed for the reaction in our experiments (five hours) was chosen on account of its being a convenient one for our purpose, but the iodine absorption was not complete at the end of that time. On allowing the absorption to proceed for twelve hours we obtained numbers varying from 140 to 151 per cent.

We find, like Thomson and Ballantyne, that the iodine absorptions of genuine seal oils vary within wider limits than was formerly thought to be the case, the maximum and minimum numbers in the six samples examined by us differing by as much as 11 per cent.

Oil.	Colour.	Specific gravity 15°/15°.	Insoluble fatty acids.	Melting-point of fatty acids.	Iodine absorption.	Bromine absorption.	Total acid number.	Saponification equivalent.	Free fatty acids (as oleic).	Reichert's test.
			Per cent.							
Pale seal, No. 1	Very pale.	0·9258	93·8	22·0° C.	136·4	77·2	19·6	286	1·13	0·22
Pale seal, No. 2	Very pale.	0·9249	93·6	22·0° C.	133·0	77·6	19·4	289	1·05	—
Pale seal, No. 3	Very pale.	0·9255	94·2	23·0° C.	141·0	79·8	19·04	294·6	0·98	0·07
Tinged seal ..	Yellow.	0·9263	92·8	23·0° C.	137·4	80·0	19·6	286	1·41	—
Straw seal ..	Lt. brown.	0·9261	93·5	22·5° C.	139·0	78·2	—	—	4·09	0·13
Brown seal ..	Dark ,,	0·9226	94·0	23·0° C.	129·5	69·6	19·24	291·5	19·95	—
		Sp. gr. 20°/20°.								
"Blown" seal	Very dark.	0·9815	73·4	23·0° C.	78·2	55·5	22·1	253·8	16·5	0·45

Bromine Absorption.—For the determination of the amount of bromine with which 100 parts of the oil can combine, the method proposed by Mills and Snodgrass (*Journ. Soc. Chem. Ind.*, 1883, p. 435) was used. About 0·15 grm. of the oil was dissolved in 25 c.c. of carefully dried and recently distilled carbon disulphide. An excess of a solution of bromine in the same solvent was added, and the mixture was allowed to stand in a dark place for fifteen minutes. At the end of this time an excess of potassium iodide was added, and the liberated iodine was determined by titration with a standard solution of sodium thiosulphate. In some of our experiments pure dry carbon tetrachloride was substituted for the carbon disulphide as a solvent for both the oil and the bromine. It will be seen that our numbers are considerably higher than those obtained by Mills and Akitt (*Journ. Soc. Chem. Ind.*, 1884, p. 366). The two numbers given by these chemists for samples of "pale" and "dark" seal oils respectively are 57·34 and 59·92 per cent of bromine absorbed. So far as we know no other bromine absorptions of seal oil have been recorded, the two numbers above mentioned being the only numbers quoted by Wright in his recent standard work on the fixed oils and fats.

The numbers given by us in the above Table (which are the mean of very many experiments) are more in accordance with the iodine absorptions of seal oils than those of Mills and Akitt, and are also more in accordance with the bromine absorptions of other oils recorded by these chemists in their interesting paper on this subject. On increasing the time during which the bromine was allowed to remain in contact with the oil from fifteen minutes to one hour, we obtained numbers as high as 89 per cent of bromine absorbed, but in these experiments the hydrobromic acid formed showed that substitution as well as addition products had been formed.

We find that it is more difficult to obtain concordant bromine absorptions than concordant iodine absorptions, variations of the experimental conditions having apparently a greater influence on the former results than on the latter. We may add that the bromine used by us in these experiments had been very carefully purified by us before use. All the oils examined united with bromine with extreme readiness.

Total Acid Number.—In this column we give numbers which represent the amounts of caustic potash required for the saponification of 100 parts of the oil. Our results are in accordance with those of other chemists. Thomson and Ballantyne, working with four samples of oil, found numbers varying from 18·93 per cent to 19·37 per cent, whilst Stoddart and Deering (also working with four samples of oil) obtained results varying from 18·9 per cent to 19·6 per cent, which is practically identical with the range of variation that we have observed.

Free Fatty Acid.—The free fatty acid is of course not in any sense an "analytical constant," but we have given it in order to make our examination of these samples of oil somewhat more complete. The results are expressed in terms of oleic acid.

Reichert's Test.—The numbers given under this heading represent the amount of caustic potash (in grms.) required to neutralise the volatile fatty acids obtained by saponifying 2·5 grms. of the oil and then distilling after having acidified with sulphuric acid. Our numbers are lower than those given by Schädtler, but the results have very little analytical importance. We have made the determinations merely in order to ascertain what difference the "blown" seal oil would exhibit in this respect.

Blown Seal Oil.—For this sample of oil we are indebted to the courtesy of Messrs. J. and D. Hamilton, of Glasgow, who inform us that the oil was blown for a period of 45 hours at a temperature of 190° F. The oil was very dark in colour and extremely viscous. Ordinary seal oils have considerably lower viscosities than rape oil (the above six samples had viscosities at 15° C. of 60—64, rape oil at the same temperature being taken as 100), whereas at 50° C. a certain volume of this "blown" oil took 63 times as long to flow through a certain orifice as the same volume of rape oil. On referring to the numbers given in the Table it will be seen that they differ considerably from those given by the natural oils. The specific gravity is in the first place very considerably higher. The percentages of insoluble fatty acids are very much lower, as are also the percentages of bromine and iodine absorbed by the oil. The total acid number is, on the other hand, higher than in the unblown oils.

The general character of these results is entirely in accordance with those obtained by Thomson and Ballantyne (*Journ. Soc. Chem. Ind.*, 1892, p. 506) in a series of experiments made with samples of "blown" sperm, cotton-seed, and rape oils, and point, as one would expect, to changes of a very similar nature having taken place.

The precise character of these changes yet remains to be investigated.

Chemical Laboratory,
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FLAME SPECTRA AT HIGH TEMPERATURES.*

By W. N. HARTLEY, F.R.S.

Part II.—The Spectrum of Metallic Manganese, of Alloys of Manganese, and of Compounds containing that Element.

The spectrum of manganese has been the subject of much investigation; the spark spectrum was examined by Huggins, Thalén, and Lecoq de Boisbaudran; the arc spectrum was studied by Ångström, Thalén, Cornu, Lockyer, also Liveing and Dewar; the flame spectra obtained from compounds of manganese were investigated by Simmler, Von Lichtenfels, Lecoq de Boisbaudran, and Lockyer, while Marshall Watts has given us accurate measurements of the wave-lengths of lines and bands observed in the spark and oxyhydrogen flame spectra of spiegeleisen, manganese dioxide, and other compounds of this metal.

When investigating the spectrum of the Bessemer flame, I found it necessary to compare the spectrum of elementary manganese under different conditions with that of its oxide when heated in the oxyhydrogen flame. Comparative experiments were made also with various alloys, as spiegeleisen, silico-spiegel, ferromanganese, tool steel, and malleable nickel which contains manganese; also with compounds containing similar quantities of metal.

Metallic manganese was prepared by the electrolysis of manganese chloride, from which all other metals had been carefully separated. One preparation of pure manganese oxide was precipitated from a solution of potassium permanganate by the action of alcohol and a small quantity of sulphurous acid. Other specimens were precipitated from solutions of potassium permanganate by the addition of hydrogen peroxide. By this treatment pure manganic oxide containing only traces of potash was obtained. From one preparation even the potassium was removed.

Photographs of the spectra of metallic manganese and of manganic oxide were taken and compared. They were also compared with the spectra of the alloys of manganese. The periods of exposure varied from a mere flash in the case of spiegeleisen when being poured into a Bessemer converter, to thirty minutes, and even as much as eighty minutes with manganic oxide.

The leading features of the spectra of manganese and manganese oxide are the same, but they differ in detail, as may be observed by comparing the wave-lengths of the lines and bands in their respective spectra.

It will be readily understood that the bands can be

* A Paper read before the Royal Society, June 14, 1894.

measured with far less accuracy than the lines, and that they are subject to some degree of variation in width, according to variation in the time of exposure and the temperature.

A striking group of lines, the most persistent in the whole of these spectra, is situated in the violet. The following experiments were made:—

4036·5	4034·9	Angström, also Cornu.
4032·0	{4032·9 / 4031·8}	Angström.
4029·5	4029·4	Angström.

Another line is just visible about 4031·8, but it is so close to 4032·0 that it could be discerned only when the extreme points of three very strong lines were examined, and the plate was in perfect focus for that region. The whole group of lines appears as two bands very closely adjacent, or in the manganese oxide spectrum as one band with the centre appearing as if reversed, the less refrangible edge of the band being very strong and sharp, the more refrangible being degraded and diffuse. These lines remain after the bands in the yellow and green have disappeared from the photographs, but the result may be quite otherwise with eye observations, owing to the greater visibility of the yellow over the violet rays.

Photographs of the spectra taken with a dispersion of four quartz prisms of 60° and lenses of 15 inches in focal length are presented with the paper.

(To be continued).

NOTE ON PEMBERTON'S METHOD OF PHOSPHORIC ACID DETERMINATION AS COMPARED WITH THE OFFICIAL METHODS.*

By WILLIAM C. DAY and A. P. BRYANT.

Having occasion to make a series of determinations of phosphoric acid in Florida phosphate rock, we have used the method recently described by Mr. H. Pemberton, jun. (Chem. News, lxix., p. 286, and incidentally have made a number of comparisons between it and the official method. The following are the results:—

Gravimetric Determinations.

No. 1. From 0·7867 grm. $Na_2HPO_4+12H_2O$, obtained 0·2426 grm. $Mg_2P_2O_7$.
No. 1. From 1·1100 grms. $Na_2HPO_4+12H_2O$, obtained 0·3433 grm. $Mg_2P_2O_7$.
No. 2. From 1·0000 grm. Florida rock, obtained 0·5828 grm. $Mg_2P_2O_7$.
No. 3. From 0·3807 grm. Florida rock, obtained 0·0262 grm. $Mg_2P_2O_7$.
No. 3. From 0·4831 grm. Florida rock, obtained 0·0333 grm. $Mg_2P_2O_7$.
No. 4. From 1·0036 grms. Florida rock, obtained 0·0227 grm. $Mg_2P_2O_7$.

Determinations by Pemberton's Method.

No. 1 used 1·0737 grms. $Na_2HPO_4+12H_2O$ and 22·88 c.c. KOH solution and 1·85 c.c. acid.
No. 1 used 1·0370 grms. $Na_2HPO_4+12H_2O$ and 21·30 c.c. KOH solution and 0·80 c.c. acid.
No. 2 used 1·0000 grm. Florida rock and 41·85 c.c. KOH and 5·05 c.c. acid.
No. 4 used 1·0000 grm. Florida rock and 7·55 c.c. KOH and 3·10 c.c. acid.
No. 4 used 1·0000 Florida rock and 6·75 c.c. KOH and 5·50 c.c. acid.

Strength of H_2SO_4 used, 1 c.c. = 0·015998 grm. H_2SO_3.

Strength of potassium hydrate solution, 1 c.c. = 0·01847 KOH.

The percentages of P_2O_5 calculated from the foregoing determinations are:—

Substance.	Gravimetric.	Pemberton.
No. 1. Sodium hydrogen phosphate	19·72	19·73
No. 1. Sodium hydrogen phosphate	19·78	19·99
No. 2. Florida rock	37·28	37·22
No. 3. Florida rock	4·40	4·53
No. 3. Florida rock	4·41	—
No. 4. Florida rock	1·45	1·32

It is evident from the above figures that the agreement between the results of the two methods is as close as could be desired. Inasmuch as the Pemberton method is of extreme accuracy, is very easily carried out, and effects a great saving of time and labour over the official method, it is well worthy of extended use. We have found that the author's statement of the time required for a single determination, namely, thirty to forty minutes from the time the solution is measured out for titration, is entirely reasonable. Omitting filtration of silica makes no difference in the accuracy of the results.

* Read at the Chemical Section of the Franklin Institute, Feb. 20, 1894.

NOTE ON AN EXTRAORDINARY SAMPLE OF WATER.

By Dr. T. L. PHIPSON.

During past years I have made known in this Journal many results of analyses of waters derived from various sources, and used either for drinking or for industrial purposes. But of all the samples received of late at my laboratory, one of the most extraordinary and instructive is that of which I will now give a brief account.

A gentleman in the country sent me about four quarts of what he termed "drinking water from a new reservoir." The sample was colourless, bright and clear, had no deposit, and no odour; but it had a distinctly bitter taste and an alkaline reaction: it turned red litmus paper blue in an instant. This water, I was informed, was good for nothing. It was impossible to drink it; it cooked vegetables badly, depriving them of their colour, and when used for washing it attacked the hands.

I found that it became milky when a current of carbonic acid was passed into it, and that it contained a considerable amount of caustic lime. It yielded to analysis exactly 100 grains of lime to the imperial gallon; in other respects it was not rich in saline or organic matter.

Having followed up the subject, I learnt that no water was supplied to the house, and there was no well. The rain-water which fell upon the roof was collected, and conducted by an iron pipe into a subterranean reservoir supplied with a pump. This reservoir had been lined with hydraulic cement, which was, probably, of bad quality, and yielded up caustic lime, sulphate of lime, and other salts in smaller amounts and of less importance to the water.

I recollect that something similar occurred some years ago at the Royal Aquarium, where some fish were killed in tanks that had been treated with hydraulic cement which yielded a notable amount of caustic lime to the water.

This shows that it is important to submit such cements to a careful chemical examination before using them in fish-tanks or reservoirs destined to store water for domestic purposes.

The Casa Mia Laboratory, Putney, S.W.,
July 1, 1894.

ON THE

RECOGNITION OF HYDROBROMIC ACID.

By A. VILLIERS and M. FAYOLLE.

The qualitative detection of hydrobromic acid in presence of hydriodic acid may be effected easily when the proportion of the former is sufficiently large by employing the well-known method founded upon the action of chlorine upon the two hydracids in presence of carbon disulphide, which is successively coloured violet and then brown by the solution in this liquid of the iodine, and the bromine set at liberty, the chlorine-water being added drop by drop, agitating strongly after each addition, so as to avoid the action of an excess of chlorine upon the iodine and bromine, and the consequent production of colourless compounds.

But this procedure gives only bad results when the proportion of bromine to the iodine falls below a certain limit.

In the absence of bromine the violet colour, produced with the faintest traces of iodine, becomes more and more intense until the total iodine is set at liberty, then it turns lighter and returns exactly through its former shades, always remaining distinctly violet. It is not the same in presence of bromine. The liberation of the first portions of iodine still gives a colouration distinctly violet, but in the second phase of the operation and when there still remains hydriodic acid or an iodide in presence of hydrobromic acid or a bromide, and part of the bromine is simultaneously set free along with the iodine. On agitating the whole the bromine does not displace the iodine of the remaining hydriodic acid, at least not distinctly and completely, and we do not return by the violet shades observed at the outset and more attenuated, but a part of the bromine combines with the iodine already set free, forming a brown iodine bromide possessing considerable stability, so that the violet colour does not disappear distinctly so as to be followed by the brown colour due to the ultimate solution of the bromine in the carbon disulphide; but it passes progressively from violet to violet-brown, and then to brown. Hence, various authors, after thinking it practicable to found a method for the determination of iodine in presence of bromine upon the behaviour of chlorine with the hydracids, according to the volume of chlorine water necessary to destroy the violet colour characteristic of iodine, have ultimately abandoned the procedure, or have regarded it merely as approximative. It yields, in fact, only bad results.

The same reason is opposed to the use of this method even for qualitative purposes if it is required to detect very small quantities of bromine in presence of large proportions of iodine. The brown colour which we may obtain after the violet colour, and which enables us to detect bromine in a sufficient manner, if it is in a considerable proportion, cannot be distinctly recognised if the weight of the bromine is less than one-tenth of that of the iodine present.

In the absence of iodine the yellow colouration of the carbon disulphide is very distinct with 1 m.grm. of bromine. It is easy to obtain this colouration with a mixture of iodide and bromide containing 1 m.grm. of bromine in presence of any quantity of iodide, that is to recognise distinctly the presence of bromine when its proportion is equal only to 1-1000th, or even less of that of the iodine. It is then sufficient to eliminate the iodine entirely at the outset.

To this end we have tried the action of various reagents already suggested. Nitric and nitrous acids gave inaccurate results. Their use coloured the carbon disulphide yellow, in consequence of the solution of nitro-compounds, which it is necessary to remove by an ulterior treatment. Further, we have not been able to detect by this procedure minute quantities of bromine. Ferric chloride, on the contrary, yields results of a perfect accuracy. This reagent has been already suggested by Duflos for the determination of iodine by a procedure to which we shall soon return. In the qualitative search for bromine in presence of iodine its employment enables us to detect traces of the former in a manner very simple and very accurate.

The liquid under examination, which must be free from nitric acid, is mixed with an excess of ferric chloride free from chlorine (not colouring carbon disulphide in presence of the alkaline bromides). The proportions to be used depend on the presumed richness of the liquid in iodine, *e.g.*, to 0·1 grm. of iodine about 5 c.c. of a semi-normal solution of ferric chloride. The iodine, if present in a notable amount, separates out and crystallises quickly. The mixture is evaporated to dryness and further heated for an hour or two hours on the water-bath. The iodine is completely separated and volatilised, whilst the hydrobromic acid remains absolutely unattacked. It is taken up in a few drops of water, the iron salts are precipitated with an alkali, the filtrate super-saturated with hydrochloric acid, and chlorine-water is added drop by drop whilst agitating with carbon disulphide. The liquid instantly takes a yellow colour, and the reaction is independent of the proportion of iodine contained in the original solution.

This procedure, on account of its simplicity, may be advantageously employed even when the hydrobromic acid is present in considerable quantities, and it admits of the recognition of the bromine much more distinctly than when the iodine is not expelled.

In the general case of an analysis we operate upon the silver precipitate obtained after the elimination of hydrocyanic acid if present, as already stated in the search for chlorine. This precipitate is treated with sulphuretted hydrogen, and the liquid, after being freed from the excess of hydrogen sulphide by ebullition, is submitted to the treatment above specified.

This procedure, as also that which we have proposed for the detection of chlorine, may be compared in its precision to the spectroscopic methods.—*Comptes Rendus*, cxviii., p. 1265.

ON QUANTITATIVE SEPARATIONS OF METALS BY HYDROGEN PEROXIDE IN ALKALINE SOLUTIONS.*

By P. JANNASCH and C. J. FRANZEK.

Jannasch and McGregory have recently elaborated a method for the separation of manganese and zinc. The present authors have applied this method to the separation of manganese and nickel. A separation of manganese and cobalt is not practicable under similar conditions, since the manganese peroxide separated by means of hydrogen peroxide contains considerable quantities of cobalt.

The separation of the last-named two metals can be effected in an alkaline (potassic) solution of the double cyanides of the metallic sulphates; since from such a solution the manganese can be separated absolutely free from cobalt by means of hydrogen peroxide. This last method renders possible a separation of manganese from nickel, of manganese from nickel and cobalt, and of manganese from zinc. The success of the separations requires, however, strictly defined quantitative proportions of the reagents used, and the observance of certain precautions.

In the separation of zinc from manganese, Jannasch and Niederhofheim give a decided preference to the subjoined method, as compared with the precipitation of the manganese in a strongly ammoniacal solution containing much ammonium chloride.

* *Berichte Deutsch. Chem. Gesell.*

0·5 grm. each of manganese and zinc sulphates are dissolved in 50 c.c. of water in a large platinum capsule (provided with a lip), and mixed with 10 c.c. of a 10 per cent solution of potassium cyanide; 10 c.c. of a 25 per cent solution of potassa are then added, and the mixture is stirred with a platinum spatula until the precipitate is almost entirely dissolved. The precipitation of the manganese is now effected with from 50 to 60 c.c. of a solution of pure hydrogen peroxide, and the precipitate is heated (covered) for fifteen to twenty minutes on a boiling water bath; it is then filtered into a second capacious platinum capsule and washed with hot water. When the filtrate is quite cold, it is supersaturated with hydrochloric acid (30 c.c. of concentrated acid), poured back into a capsule of Berlin porcelain, evaporated to dryness, the residue is heated in the air-bath to 110—115° for at least half an hour, the silica (rarely absent) is filtered off, and the boiling filtrate is finally precipitated in the manner directed with sodium carbonate; the zinc being finally weighed as oxide. The weighed oxide must form a clear solution in dilute acetic acid, and any impurities present (silica and alumina) must be determined and deducted.

It must further be remembered that the precipitate of manganese, washed with hot water, may still include some potassa. Hence it is advisable to dissolve the precipitate in dilute nitric acid in presence of a little oxalic acid (not exceeding 0·3 grm.), and to re-precipitate the manganese with hydrogen peroxide in an ammoniacal solution.

Continued researches on the precipitation of different metals in alkaline solutions by means of hydrogen peroxide have led P. Jannasch (*Berichte*) to the following methods of separation:—

For the separation of lead and silver, he dissolves about 0·5 grm. each of the metallic salts in question (in this case the nitrates) in 50 c.c. water, adds 2 c.c. of strong nitric acid, and precipitates the lead in the cold as hydrated peroxide with a mixture (previously prepared) of from 15 to 20 c.c. of a 2 per cent solution of *pure* hydrogen peroxide (the commercial samples of this reagent too often contain salts of barium, sulphuric acid, silica, alumina, &c.), and 15 c.c. of concentrated ammonia to which 5 c.c. of a solution of ammonium carbonate, saturated in the cold, are further added. He waits for about ten minutes, stirring frequently, before filtering off the flocculent yellowish brown precipitate, washes three or four times with ammoniacal water, and, lastly, with pure water until a drop of the filtrate, if evaporated on the cover of a platinum crucible, leaves no residue. All these operations must be effected in the cold, and the ammonium carbonate must not be added until *after* the lead has been precipitated with hydrogen peroxide. A mixture of hydrogen peroxide, ammonia, and ammonium carbonate gives not a coloured deposit but a white precipitate which runs through the filter turbid.

All suction during filtration and washing must be avoided, but funnels should be used which filter well.

Jannasch determines the lead by weighing as oxide, using the following precautions in incineration:—

The filter, with the collected lead precipitate, is introduced whilst moist into a platinum crucible, so as to lie as closely as possible to the bottom, and the crucible, uncovered, is gradually heated in a small cup-shaped air-bath, 7·5 c.m. in depth, 5 c.m. in its lower and 7·5 c.m. in its upper diameter, in the upper part of which, at the distance of 27 to 30 m.m. from the edge, there is fixed a triangle of nickel or platinum wire, the whole being supported by a tall iron tripod. By means of an effective triple burner, gradually raising the heat, the filter may be incinerated without any danger to the crucible. If small portions of unburnt carbon remain they will easily smoulder on the introduction of dry oxygen gas, or even if they are momentarily touched with an ignited platinum spiral. A preliminary weighing can be performed as soon as the crucible is cold. The weighed oxide is then just covered with strong nitric acid, the necessary quantity of hot water is added, and evaporated down on the water-bath with occasional agitation. The dry residue is heated again in the nickel beaker until most of the nitric acid is expelled, and, lastly, the complete decomposition of the lead nitrate is effected by cautiously heating the covered crucible over a naked flame. We may then, without any fear for the platinum crucible, ignite the resulting lead oxide over a flame about an inch in height. Contaminations of silica, &c., if present, may now be determined and their weight deducted.

It is not admissible to weigh the lead oxide in a porcelain crucible, as the metallic oxides attack the porcelain seriously on ignition.

(To be continued.)

METHODS FOR MILK ANALYSIS.*

Determination of Water.

Evaporate 1 to 2 grms. of milk in a tared flat dish containing from 15 to 20 grms. of pure dry sand, or without sand, until apparently dry. Dry and heat for one hour at the temperature of boiling water. Cool in a desiccator, and weigh rapidly to avoid absorption of hygroscopic moisture.

Determination of Total Nitrogenous Matter.

Place in a Kjeldahl digestion flask a known weight (about 5 grms.) of milk, and proceed, without evaporation, exactly as described for this method under nitrogen.

Determination of Total Solids and Fat.—Babcock Asbestos Method.

Provide a hollow cylinder of perforated sheet metal, 60 m.m. long and 20 m.m. in diameter, closed 5 m.m. from one end by a disc of the same material. The perforations should be about 0·7 m.m. in diameter and about 0·7 m.m. apart. Fill loosely with 1·5 to 2·5 grms. of freshly ignited woolly asbestos, free from fine and brittle material, cool in a desiccator, and weigh. Introduce a weighed quantity of milk (3 to 5 grms.) and dry at 100° C. to constant weight for the determination of total solids. Extract with anhydrous ether until fat is removed, evaporate the ether, dry the fat at 100° C. and weigh. The fat may also be determined by difference, drying the extracted cylinders at 100° C.

Determination of Fat.—Paper-coil Method.

Coils made of thick filter paper, cut into strips 6·25 by 62·5 m.m. are thoroughly extracted with ether and alcohol, or the weight of the extract corrected by a constant obtained for the paper. If this latter method is used a small amount of anhydrous sodium carbonate should be added. From a weighing-bottle about 5 grms. of milk are transferred to the coil by a pipette, care being taken to keep the end of the coil held in the fingers dry. The coil, dry end down, on a piece of glass, is dried at the temperature of boiling water for one hour, or, better, dried in hydrogen at the temperature of boiling water, transferred to an extraction apparatus, and extracted with absolute ether or petroleum spirit boiling at about 45°. The extracted fat is dried in hydrogen and weighed.

If the milk is sour, add about 10 per cent, by weight, of strong ammonia water, and a small quantity of anhydrous sodium carbonate, correcting the results for the ammonia added.

Determination of Sugar.

Reagents.

1. *Basic Lead Acetate, sp. gr.* 1·97.—Boil a saturated solution of sugar of lead with an excess of litharge and

* Official Methods of Analysis adopted by the Association of Official Agricultural Chemists (American) at its Meeting at Chicago, August, 1893.

make it of the strength indicated above. 1 c.c. of this will precipitate the albumens in 50 to 60 c.c. of milk.

2. *Acid Mercuric Nitrate.*—Dissolve mercury in double its weight of nitric acid, sp. gr. 1·42. Add to the solution an equal volume of water. 1 c.c. of this reagent is sufficient for the quantity of milk mentioned above. Larger quantities can be used without affecting the results of polarisation.

3. *Mercuric Iodide with Acetic Acid.*—KI, 33·2 grms.; $HgCl_2$, 13·5 grms.; $C_2H_4O_2$, 20 c.c.; H_2O, 64 c.c.

Apparatus.

1. Pipettes marked at 59·5, 60, and 60·5 c.c. 2. Sugar flasks marked at 102·4 c.c. 3, Filters, observation tubes, and polariscope. 4. Specific gravity spindle and cylinders. 5. Thermometers.

Manipulation.

1. The room and milk should be kept at a constant temperature.

2. The specific gravity of the milk is determined. For general work this is done by a delicate specific gravity spindle. Where greater accuracy is required use specific gravity flasks.

3. If the specific gravity be 1·026, or nearly so, place 60·5 c.c. in the sugar flask. Add 1 c.c. of mercuric nitrate solution, or 30 c.c. of mercuric iodide solution, and fill to the 102·4 c.c. mark. The precipitated albumen occupies a volume of about 2·44 c.c. Hence the milk solution is really 100 c.c. If the specific gravity is 1·030, use 60 c.c. of milk. If the specific gravity is 1·034, use 59·5 c.c. milk.

4. Fill up to the mark in the 102·4 c.c. flask, shake well, filter, and polarise.

NOTES.—In the above method of analysis the specific rotatory power of milk sugar is taken at 52·5, and the weight of it in 100 c.c. solution to read 100 degrees on the cane-sugar scale at 20·56 grms. This is for instruments requiring 16·19 grms. sucrose to produce a rotation of 100 sugar degrees. It will be easy to calculate the number for milk sugar, whatever instrument is employed.

Since the quantity of milk taken is three times 20·56 grms., the polariscopic reading divided by 3 gives at once the percentage of milk sugar when a 200 m.m. tube is used.

If a 400 m.m. tube is employed, divide the reading by 6; if a 500 m.m. tube is used, divide by 7·5.

By using a flask graduated at 102·4 c.c. for 60 c.c. no correction for volume of precipitated casein need be made. In no case is it necessary to heat the sample before polarising.

Alternate Method for Sugar.

The sugar may also be determined, either gravimetrically or volumetrically, by alkaline copper solution, as described under sugar analysis.

Determination of Ash.

In a weighed dish put 20 c.c. of milk from a weighing bottle; add 6 c.c. of HNO_3, evaporate to dryness, and burn at low red heat until ash is free from carbon.

The International Congress of Applied Chemistry, to be held at Brussels, August 4th to 11th, 1894.—In our issue of December 22nd, 1893, p. 302, we drew attention to the above-mentioned Congress, which will be held at Brussels next August. We have now had a further communication from the Secretaries, in which we note that His Majesty King Leopold II. has appointed a number of distinguished gentlemen to act as a "Committee of Patronage," for the purpose of furthering the work of the Congress and of the conferences which will be held in connection therewith. We may remind our readers that, besides the serious work of the Congress, there will be a number of excursions to places of interest, as well as other social functions, which will all combine to make an enjoyable autumn holiday.

ON THE ORIGIN OF GOLD NUGGETS.*

By A. LIVERSIDGE, M.A., F.R.S.,
Professor of Chemistry in the University of Sydney.

(Continued from p. 304).

Gold in Natural Waters.

VERY little is accurately known as to the solution of gold by natural waters; we know, it is true, that gold has been deposited from solution, and we also know that its deposition from such is still going on, and several references are made to its deposition in this paper, but the search for gold in meteoric and mine waters has not met with satisfactory results; the analyses which have been made do not absolutely prove that gold is present in solution—the presence of gold has been detected, but it may have been held there mechanically. Accordingly I have thought that it would not be amiss to give a brief *resumé* of the papers which I have come across upon this matter.

In the case of sea water, however, E. Sonstadt published a communication in the CHEMICAL NEWS (vol. xxvi., p. 159) upon the presence of gold in sea water, and stated that he had not determined the amount, but that it was less than 1 grain per ton. A letter appeared from him upon the same subject on March 11th, 1892 (CHEM. NEWS, vol lxv., p. 131), confirming his previous statement, both as to its presence and to the smallness of the amount, "being far less than 1 grain to the ton."

The presence of gold (and silver) in sea water as alleged by Sonstadt is confirmed by the presence of gold and silver in the sheathing from old vessels and piles—one specimen which I had examined, from a vessel which had long traded along the Australian coasts, contained traces of gold and silver, but in much larger proportion than one would expect in Muntz metal; but as none of the unexposed metal could be obtained, the difference or increase (if any) could not be determined.

The sheathing was dissolved in pure sulphuric acid, and the insoluble residue examined for gold and silver; with the lead sulphate was a comparatively large quantity of iodine, the latter evidently derived from the sea-water. Lately I have obtained, through the kindness of Mr. C. W. Darley, Engineer-in-Chief for Harbours and Rivers, specimens of sheathing from piles in various places along the coasts of New South Wales, so that the age and conditions of exposure of the sheathing are known; and he has also been good enough to have plates of Muntz metal attached to piles in the following places, viz., at Newcastle and on the Richmond, Clarence, Macleay, Shoalhaven, and Moruya Rivers; and a section through the plate has been sent to me to determine the silver and gold before immersion in sea-water, so that when the immersed plates are analysed, after a certain number of years time, any accumulation of gold and silver can be rigidly determined.

One of the earliest writers in Australasia, the Rev. W. B. Clarke, M.A., in his "Southern Gold Fields" (Sydney, 1860), in a letter to the *S. M. Herald*, 15th June, 1858, says (p. 55), "It, *i.e.*, gold, is elaborated by vegetable growth in soils where there are no pretended geological indications; it is found occasionally in rain-water; it may, for anything I know to the contrary, exist in the air, vapourised and afloat, as reguline."

Gustav Bischof, in his "Elements of Chemical and Physical Geology" (*Car. Soc.*, 1859, vol. iii., 534), says, "A silicate of gold may be prepared artificially, and it appears that under certain circumstances it may be dissolved in sensible amount. The . . . quartz associated with gold certainly originates from the decomposition of silicates in rocks, and it may be conjectured that the gold has the same origin, possibly existing as silicates."

* A Paper read before the Royal Society of New South Wales, September 6, 1893.

I have verified Bischof's statement by digesting gold-leaf with sodium silicate and potassium silicate solutions under a pressure of 90 lbs. to the square inch, and found that the solution gave a brown precipitate with oxalic acid, and that this acquired the metallic lustre and colour of gold under a burnisher.

The reduction of gold chloride in solutions of sodium and potassium silicates, also mentioned by Bischof, was verified, but I do not attach much importance to these experiments, for gold chloride is so easily reduced that its reduction is brought about by almost anything; the fact that gold is dissolved by sodium silicate is a matter of much greater importance. The solution in sodium silicate turned blue in about thirty minutes; that in potassium silicate took a longer time, and the separated gold was of a reddish tint.

J. Cosmo Newbery states that an amethystine colour is sometimes seen in quartz reefs and in wash dirt. Aplin, at Beechworth, Victoria, found that such clay, after exposure to light, lost its colour, and showed the presence of gold although none was visible before; a successful miner, Clement, observed the same thing at Maldon. This appears to indicate that the clay was moistened with a solution of a gold salt. No chemical examination was, however, made.

Lock (p. 558), quoting from Prof. Hutton "On the Thames Gold Field," says, "Of the time when the veins were first charged with gold, Hutton can offer no opinion; but there are one or two facts which make it appear probable that gold is still in circulation through the rocks. . . . In the Niau claim, above the Hokianga, on the Karaka, open quartz veins are seen partly filled with black humus that has filtered down from the vegetable soil above, and this humus, on being carefully washed, yields fine gold, which Hutton supposes had been precipitated from solution by the organic matter of the humus."

C. Dolter, "Solubility of Minerals" (*Monatsh.*, ii., p. 149), found that gold at 200° C., in a sealed tube with a 5 per cent solution of Na_2CO_3 or Na_2SiO_3, is dissolved to the extent of 1·5 per cent of the weight of the gold taken.

Bischof also found that gold sulphide is slightly soluble in meteoric waters, and still more soluble in a saturated solution of hydrogen sulphide; and that it is also slightly soluble in persalts of iron.

Newbery tested this by dissolving gold sulphide in a weak solution of an alkaline bicarbonate, and found, on introducing a chip of wood and a cube of pyrites, that the gold was deposited on the pyrites. (See his paper "On the Formation of Nuggets," *Roy. Society, Victoria*, 1868.)

I find that gold-foil is attacked by a strong solution of sodium sulphide; in nine days a fillet of gold-foil, exposing about four square inches of surface, and weighing 0·6181 grm., lost 0·0021 grm. Gold-leaf treated with sodium sulphide still more readily yielded a solution containing gold.

R. Daintree, in his "Geology of the Ballan District, Victoria, 1866," says, "I had long come to the conclusion that most, if not all, the gold in the quartz reefs was derived from the rocks in which these reefs occur. That the strata themselves received their supply of gold at the period of their deposition from the ocean in which they were deposited. That the organic matter and the gases generated therefrom on decomposition, sulphuretted hydrogen, &c., were the cause of the precipitation; and that the amount of metallic deposit was in proportion to the amount of organic matter deposited with the organic sediment."

Sir W. Logan says (quoted by Daintree), "The observations among the gold-bearing rocks of the Southern States seem to show that the precious metal was originally deposited in the beds of various sedimentary rocks, such as slates, quartzites, and limestones, and that by a subsequent process it has been, in some instances, accumulated in the veins which intersect these rocks."

An additional proof of the solubility of gold in natural waters is given in "A Treatise on Ore Deposits," by Bernhard von Cotta. Translated from the second German edition, New York, 1870, p. 198, says, "The gold at Eisenberg, near Corbach, Rhine, occurs partly in the clefts of the quartz siliceous slate in thin dendritic incrustations; or (and this is the most common occurrence) it encrusts the very small rhombohedrons of spathic iron, which are found on the limestone incrustations of the clefts; these consequently have the appearance of gold crystals."

Orville A. Derby, in a paper on "Peculiar Modes of Occurrence of Gold in Brazil" (*Am. Jour. Sci.*, Dec., 1884, p. 440), affords still another example of the recent deposition of gold from solution. In this paper an account is given of a specimen of gold on limonite from Ponte Grande, Sabara, Minas Geraes. The limonite is botryoidal, lustrous, in parts of an iridescent bronzy colour, and in others black and brown, and on various parts of the specimen are minute detached films of gold. The author points out that these films of gold have apparently been deposited from solution upon the limonite, which is also a mineral of aqueous origin."

Similar thin films of gold, as thin as gold-leaf, are seen on the limonite at Mount Morgan, Queensland, and upon quartz at Oura, near Wagga Wagga, New South Wales.

J. Cosmo Newbery, B.Sc., in a paper "Upon the Mineral Waters of Victoria (*Trans. Roy. Soc. Vict.*, 1867, p. 278), gives the analyses of several mineral waters, and amongst them those of certain auriferous quartz mines of Maldon, which are remarkable for the large quantity of potassium chloride present, but gold in solution does not appear to have been met with. He investigated the question of the presence of gold in the waters of gold-mines, and found gold in mine timbers, boiler deposits, &c., but stated that it was difficult to make sure that the gold had not found its way in mechanically. Other observers also have failed to prove the presence of gold in solution in mine waters by chemical tests.

Plates of copper connected with a battery were placed in mine waters, but although gold was found on the crust which coated them, the trial could not be relied on, as the copper was not tested before the experiment was started.

The following quotation from Sterry Hunt is still another proof that gold does exist in solution in natural waters:—"I have in my possession a portion of a small trunk taken from the mud of a spring in the province of Ontario, in which the yet undecayed wood of the centre is seen to be incrusted by hard and brilliant iron pyrites. In like manner the trees found in the New Jersey sandstone became incrusted with copper sulphide, which as decay went on, in great part replaced the woody tissue. Similar deposits of sulphides of copper and of iron often took place in basins where the organic matter was present in such a condition or in such quantity as to be entirely decomposed, and to leave no trace of its form, unlike the examples just mentioned. In this way have been formed fahlbands and beds of pyrites and other ores. The fact that such deposits are associated with silver and with gold leads to the conclusion that these metals have obeyed the same laws as iron and copper. It is known that both persalts of iron and soluble sulphides have the power of rendering gold soluble, and its subsequent deposition in the metallic state is then easily understood."—"Chemical and Geological Essays," 2nd edition, 1879, p. 232.

J. C. Newbery analysed similar recent tree trunks from the Victorian Gold Fields, converted into pyrites, and found gold present.

In 1876, when in New Zealand, I collected some iron pyrites, from a hot spring at Taupo, which was being deposited upon some twigs and branches of wood; the

wood was much decayed, black, and quite rotten, but it still retained its form and character. The iron sulphide was, on assay, found to contain traces of gold, which must have been in solution in the water.—(*Journ. Roy. Soc. N. S. Wales*, 1877, p. 264) The waters from the hot springs occurring in different parts of New Zealand have been carefully analysed from time to time by Mr. Skey, F.C.S., Government Analyst, but I think that gold has not been detected in any of them, although we know it must be there, because it is contained in the pyrites deposited from the waters, by decaying organic matter reducing the sulphates in solution.

The following extract, from the "Mining and Metallurgy of Gold and Silver," by J. Arthur Phillips (footnote, pp. 10, 11), is given because it refers to the recent deposition of gold from solution, and apparently also by volatilisation :—

"The moulds of cubical crystals of iron pyrites are requently found in the quartz of auriferous veins, and more particularly so near the surface, thus showing that the formation of the pyrites must have been as old as that of the vein itself. In such cases, although the iron has often been entirely removed by chemical action, the cavities left sometimes contain finely divided gold, obviously liberated by the decomposition of pyrites. The gold contained in crystallised pyrites enclosed in quartz is readily rendered apparent by placing the specimen, for a few hours, in a warm place, in nitric acid, by which the pyrites is dissolved, and finely powdered or filiform gold will partially occupy the resulting cavities. With regard to the age of auriferous quartz veins, it has been already shown that many of them must evidently be of comparatively recent date; but in some cases the deposition of gold-bearing quartz would appear to be taking place even at the present time. At Steamboat Springs, near Virginia, in the State of Nevada, and in other localities on the Pacific Coast, numerous parallel deposits of quartz, assuming the form of veins, are taking place along a line of boiling springs now in a state of great activity. The quartz from this locality exactly resembles that of the ordinary auriferous quartz veins of California, and, besides small quantities of iron and copper pyrites, contains oxide of iron and traces of manganese. On making an examination of this quartz for gold and silver, we were unable to find an appreciable quantity of either of these metals; but Mr. Laur, who made a similar investigation of this quartz, succeeded in finding specimens containing small quantities of gold.—(*Annales des Mines*, Sixième Série, iii., p. 421.) These facts would, therefore, not only tend to lead to the conclusion that auriferous veins are under certain conditions deposited from siliceous solutions, but also to explain the action by which many of the slates of the auriferous period may have become metamorphosed and silicified."

We are indebted to Dr. Oxland, formerly manager of the works belonging to the Borax Lake Company, Lake County, California, for the following note on the occurrence of gold and silver in that locality :—

"In the Sulphur Bank at Borax Lake sulphur is constantly in course of formation, with the evolution of aqueous vapour, carbonic acid, and boracic acid, but without any sulphuretted hydrogen, which might have been expected to be present. The smell of carbonic acid is remarkably pungent. The gaseous matters issuing from the "Soffioni" in gentle blowers are usually at the temperature of about 95° F. They appear to be the agency by which gold, silver, mercury, and iron are brought up from below and deposited in cavities near the surface. Sulphur is deposited on the sides of the cavities, either in groups of crystals or in highly translucent amorphous masses of a beautiful light lemon-yellow colour. Sometimes the sulphur is intermixed with cinnabar, but more frequently with very fine crystals of iron pyrites, and with pulverulent silica in masses blackened by some hydrocarbon which is difficult to isolate. The iron pyrites may be separated by dissolving off the sulphur with bisulphide of carbon, and washing off the silica with water. It is found associated with silver and a trace of gold.

"On the sides of the cavities of the blowers, gelatinous silica is sometimes found coating opalised silica in varying degrees of induration, according to its depth from the surface, presenting examples of opal or hydrated silica in its various stages of formation, from gelatinous silica up to the hardest opal. The indurated silica is sometimes colourless, but is more frequently permeated with cinnabar or iron pyrites, and blackened by the tarry matter before alluded to. Sometimes, from a diffusion of cinnabar throughout the mass in minute quantity, it is delicately tinted of a pinkish colour. The cinnabar is also found in striæ, and occasionally even in veins and concretionary masses of some thickness. Where the bituminous matter occurs in the largest quantity, and the mass is quite black and friable, cinnabar is replaced by metallic mercury.

"In another locality of similar character, about ten miles distant, gold has been found with cinnabar in crystalline masses of some size. In the same place, a vein of apparently compact quartz, about 10 inches in thickness, was found to be so friable that it could be easily taken out with the hand in small conchoidal fragments, most of which rapidly fell into fine powder. From its great resemblance to a vein occurring in the Mexican mine, Virginia city, which is many feet in thickness, and contains 20 to 30 dollars of gold and silver to the ton, attention was drawn to it, and it proved, on being assayed, to contain with a trace of gold to the value of 15 dollars per ton.

"These phenomena present indubitable evidences of the volatility of gold, silver, mercury, and iron, in presence of aqueous vapour associated with sulphuretted hydrogen, carbonic acid, and boracic acid. Whether the contemporaneous association of these substances may produce a definite compound possessing peculiar powers of solution and volatilisation under the influence of elevated temperature, although probable, yet remains to be proved."

(To be continued.)

PRESENTATION TO DR. TILDEN AT MASON COLLEGE.

At the Chemistry Theatre of the Mason College there was a numerous gathering, on the 25th ult., of past and present students, to bid farewell to Dr. Tilden, and to congratulate him on his appointment to the Royal College of Science. The esteem in which the Professor is held was displayed in a marked manner during the proceedings, which were of an extremely interesting and enthusiastic character. One of the old pupils (Mr. A. J. Cooper) presided; and though the occasion was the outcome of the wish of past and present students to do honour to Dr. Tilden, there were several professors and visitors present who echoed the kindly sentiments which pervaded the remarks of the chosen spokesmen.

Mr. Cooper said that in losing Dr. Tilden the College was losing a mainstay—one who had in great part given it the name it now possessed. (Applause.) In him they had a ripe and accomplished scholar, a polished gentleman, an efficient teacher, and one who sympathised with the difficulties of the students. (Applause.) He had never failed to inculcate the principles of rectitude, industry, and courtesy. Not only were his lectures characterised by the most perfect lucidity, but one was struck by the great enthusiasm he threw into his subjects. While they all deeply deplored his departure, they all wished he might be spared many years to continue his labours in another sphere.

Mr. Rose, on behalf of the present science students,

added his testimony to the work done by Dr. Tilden, and the esteem in which he was held.

Mr. Emanuel, speaking from the medical side of the College, assured Dr. Tilden of the profound respect and admiration he and his fellow students entertained for the Professor who had done so much in establishing the reputation of the institution as a science college.

One of the lady students (Miss Bowley) spoke of the unvarying kindness shown by Dr. Tilden to the students, and Mr. Miller pointed to the Professor's investigations in the world of exact science, and said that the influence of his teaching at the College would be felt far outside the institution itself.

Principal Heath remarked that it was essentially a student's occasion, and he could speak as perhaps one of Dr. Tilden's oldest students in that room. Some eighteen years ago Dr. Tilden was Master at Clifton College, and he (Professor Heath) was a boy in his class, so that he could cordially second the sentiments which had been given expression to. As a colleague he was able to congratulate Dr. Tilden upon that splendid meeting. He had had a long and honourable career in connection with that College, and his influence would be felt in every department of its work. He had conferred distinction upon it alike by his remarkable personality and his scientific labours. It remained for a leave-taking assembly of that kind to mark the real affection which the students had for their Professor. (Applause.) On behalf of the staff, he congratulated Dr. Tilden on his appointment, and hoped that in his new career he would have every success and happiness. (Loud cheers.)

Mr. C. J. Levi, as Chairman of the Chemical Society, of which the Professor is President, read an address of farewell and congratulation, and uncovered a beautiful silver bowl, which he presented to Dr. Tilden as a small mark of the esteem and appreciation of the members of the Society.

Dr. Tilden, who was enthusiastically cheered, briefly returned thanks. That moment, he said, was a proud one to him, and a trying one too. It revived in him the deep feeling of regret which he entertained three months ago at the prospect of a severance from that College. The matter had been settled so long that he had got into the way of contemplating the change with resignation, but that afternoon's proceedings had made him feel as keenly as ever how very strong were the ties that bound him to his work and friends in Birmingham. Fourteen years ago he came to Birmingham quite a stranger, at a time when there was no science college actually opened. His three colleagues—Professors Hill, Poynting, and Bridge (applause)—were appointed with him as the first four Professors of the College, when the building was quite empty. In the first session they had some eighty students between them, and those days were exceedingly happy. He then knew every student in the College personally. Now things were changed, and he regretted that there were many faces in the College to which he could attach no names. That, of course, was the natural consequence of the growth and development and the splendid success, he might say, of the College. Those first Professors had unusual privileges and responsibilities. They were naturally given a free hand. They had no traditions to live up to, no standard to go by except that which they themselves set up. They were entrusted with the great duty, the heavy responsibility, of creating their several departments and building up the life of the College, and setting up standards of teaching and conduct which would serve for their successors. How far he in his department had been successful it was not for him to say. He felt, however, that in their kindness that afternoon the students present had overrated his services. (No, no.) He had enjoyed his teaching and his work in that College, and he felt keenly how much he owed to the able assistance of those with whom he had been associated; to Dr. Morris, who was now engaged in admirable scientific work in London; to his successor, Mr. Turner, who was an authority on certain departments of metallurgy—(applause),—and to Dr. Nicol. (Applause.) For thirteen years Dr. Nicol had been his right hand, and a more faithful, loyal, and able coadjutor no man could have had. (Applause.) Dr. Tilden expressed the hope that he should often meet some of his old friends from Birmingham, and alluded to the high qualifications and ability of the gentleman who was to succeed him as Professor of Chemistry.

A vote of thanks was accorded the chairman, and three hearty cheers for Dr. and Mrs. Tilden brought the pleasing ceremony to a close.

PROCEEDINGS OF SOCIETIES.

ROYAL INSTITUTION.

Mr. Ludwig Mond, F.R.S., has made a proposal to the Managers of the Royal Institution of Great Britain, to convey to the members of that Institution the freehold of No. 20, Albemarle Street, to be held by them for the purpose of a laboratory to be named "The Davy-Faraday Research Laboratory of the Royal Institution," and for the purpose of providing increased accommodation for the Institution.

The Managers, at their meeting on the 2nd inst., most cordially and gratefully accepted this munificent gift made in the communication from Mr. Mond, of which the following is an extract:—

"In the year 1843 a proposal was made to establish at the Royal Institution a School of Practical Chemistry, which was not only to give practical and systematic instruction to students, but was also to provide a place where original researches could be conducted by individuals skilled in manipulation, and where the professors could work out their problems by the aid of many qualified hands.

"This proposal was submitted by the Managers of the Royal Institution to Professors Faraday and Brande, who expressed their strong approval of the end proposed, and their desire that it might be carried out at the Royal Institution, 'if it could be done well.' But, on a closer examination of the limited space within the walls of the Institution, it appeared impracticable to afford accommodation for carrying out the proposed scheme.

"In 1846 the Royal College of Chemistry was founded, and since that time numerous schools for the teaching of practical chemistry have been established all over the country. These, however, only cope with the first part of the scheme recommended in 1843, while as to the second part, viz., founding a laboratory for the carrying out of independent researches, no adequate provision exists in England up to this date, although the need for it was so strongly felt so many years ago, and its importance for the advancement of science so forcibly dwelt upon by the promoters of the scheme and by such men as Faraday and Brande.

"I have felt that the need for such a laboratory has become greater and greater since the work of the scientific investigator has become more and more subtle and exact, and, in consequence, requires instruments of precision and a variety of facilities which a private laboratory can only very rarely command; and surely this need exists nowhere to a greater extent than in England, and nowhere can such a laboratory be expected to bear more abundant fruit than in this country, which possesses such an unrivalled record of great scientific researches, which have emanated from private laboratories not connected with teaching institutions, and amongst which the laboratory of the Royal Institution stands foremost, and has kept up its reputation for nearly a hundred years.

"It has been my desire for many years to found a

public laboratory which is to give the devotees of pure science, anxious and willing to follow in the footsteps of the illustrious men who have built up the proud edifice of modern science, the facilities necessary for research in chemistry, and more particularly in that branch of the science called physical chemistry.

"I have come to the same conclusion as the promoters of the scheme of 1843, viz., that such laboratory would still have the greatest prospect of success under the ægis of the Royal Institution, that in fact it would be the consummation of the work which this great Institution has been fostering in its own laboratory, with such remarkable results, by the aid of the eminent men whose services it has always been fortunate enough to procure.

"As only want of space prevented the Royal Institution undertaking this task fifty years ago, I took the opportunity which offered itself last year of acquiring the premises, No. 20, Albemarle Street, adjoining the Institution. This property I found very suitable for the purpose of such a laboratory, and large enough to afford, besides, facilities to the Royal Institution for a much needed enlargement of its present laboratory and its libraries and reception rooms, which I should with great pleasure put at the disposal of the Institution.

"Being convinced that the Managers of the Royal Institution will give all the encouragement and aid in their power in the foundation and working of such a research laboratory, I hereby offer to convey to the Royal Institution the freehold of No. 20, Albemarle Street, and also the lease I hold from the Institution of premises contiguous thereto, to be held by them for the purpose of a laboratory, to be named 'The Davy-Faraday Research Laboratory of the Royal Institution,' and also for the purpose of providing increased accommodation for the general purposes of the Royal Institution, as far as the available space will allow, after providing for the requirements of the research laboratory.

"I also offer to make, at my own expense, all structural alterations necessary to fit the premises for these purposes, and to equip the Davy-Faraday Research Laboratory with the necessary apparatus, appliances, &c., and to make such further adequate provision as will hold the Royal Institution free from all expense in connection with the premises and the working of the said laboratory. . . .

"I am aware that my offer will not provide for the third object of the scheme of 1843, viz., to enable the professors to work out their problems by the aid of many qualified hands; but I trust that if the laboratory which I offer to found proves successful, others will come forward who will supply the means for attaining this end, by the foundation of scholarships and bursaries to qualified persons willing to devote themselves to scientific work and not in a position to do so without assistance."

PHYSICAL SOCIETY.

Ordinary Meeting, June 22nd, 1894.

Prof. W. E. AYRTON, F.R.S., Past President, in the Chair.

MR. LARMOR was elected a member of the Society.

Captain ABNEY, before exhibiting his "*Photographs of Flames*," demonstrated that a candle flame contains solid particles by passing a beam of polarised light through it, the track of the beam through the flame being clearly seen in one direction, whilst in a direction at right angles it was practically invisible. The same thing was also shown by passing the light through a turbid liquid. Photographs of Argand and candle flames with pencils of sunlight and electric light passing through, were then exhibited, showing similar phenomena.

Several series of photographs of flames of candles and various forms of gas burner taken with diminishing exposures, were then shown in order to illustrate the different luminosities at different parts of the flame. Those taken with long exposures showed the bright parts nearly equally white, but as the time of exposure diminished only the most luminous portions were recorded on the plate. From the photographs the author concluded that when used with a slit as a photometric standard, the Argand burner was unsuitable, for portions of different luminosity come into view when the slit is approached or receded from. The ordinary fish-tail burner was better in this respect.

Questions were asked and remarks made by Prof. S. P. Thompson, Prof. Perry, and Mr. Trotter, in reply to which Capt. ABNEY said drop shutters, with slits from 1 inch to $\frac{1}{10}$th inch wide, had been employed, and some of the exposures were only a few thousandths of a second. The displacement caused when the object was not stationary could easily be allowed for when the velocity of the shutter was known.

Prof. O. HENRICI read a paper on "*An Elementary Theory of Planimeters.*"

Considering the generation of areas by the motion of straight lines, the author defined the sense in which such areas are to be taken. Choosing the positive sense of a line, O T, of variable length as outwards from the centre O, about which it turns, and the positive direction of rotation as counter-clockwise, the following rule for determining the sense of an area was given. Imagine yourself standing at a point, P, and looking along the positive sense of O T whilst it passes over P, then the area near P will be swept out in *a positive sense if O T crosses you from right to left*, otherwise it will be negative. Applying this rule to closed curves of any shape, it was shown that if T goes once round the boundary, any area outside the curve was necessarily swept over as many times in the negative sense as in the positive sense, therefore these areas cancelled, and also that the sense of any part of an area depends on the sense of its boundary.

Passing on to the consideration of areas generated by a line (or rod) of fixed length, which moves anyhow in a plane and returns to its initial position, Prof. Henrici showed by taking instantaneous centres, that the same rule regarding the sense of the areas holds, and that the area generated by the rod is equal to the difference between the areas of the two closed curves traced by its ends. In the particular case where one end of the rod moves forwards and backwards along the same path, the area swept out by the rod is equal to that of the closed curve traversed by the other end.

This is the theory of Amsler's planimeter, for the area of the curve whose boundary is traversed by the tracer is the same as that swept out by the rod carrying the tracer when the pole is outside the closed curve. By resolving small motions of the rod in two component parts, a translation parallel to itself, and a rotation about the point in which the plane of the registering wheel cuts the rod, the author showed that the areas swept out by the translations were registered by the wheel, whilst the sum of those generated during the rotations cancel. Cases where the pole is inside the curve were next considered, and the constant then to be added to the wheel reading determined.

Instead of registering the translation by a wheel whose axis is parallel to the rod, a knife-edged wheel which slides and turns freely on an arm perpendicular to the rod, would serve the same purpose. This is the principle of Hine and Robertson's planimeter. In the actual instrument, however, the arm is inclined at about 10° to the rod, and is therefore inaccurate.

In the "Hatchet" planimeter a bent rod terminates at one end in a tracing point, and at the other in a convex knife-edge or "keel," whose plane contains the point. The area of the curve, whose boundary is traversed by the point, is approximately equal to twice that of the sector included between the initial and final positions of the rod. The approximation results from the fact that the area of the curve traced by the keel is not zero.

At the meeting the question of reducing the area of the keel curve was discussed at some length, the author showing that in the case of a curve symmetrical about a line, it was possible to reduce this area practically to zero. Even for unsymmetrical curves, one could obtain a symmetrical one of double the area by drawing a line cutting the curve and supposing the area turned over about this line.

Prof. PERRY enquired if the author's conclusion was that the Hatchet planimeter and the Hine and Robertson instrument were inaccurate? If so, he was at a loss to understand why the latter gave results more nearly correct than Amsler's.

Mr. BLAKESLEY pointed out that if both arms of a jointed planimeter be simultaneously moved over curves the total reading should give the sum of the two areas traced out, if taken in the proper senses.

Mr. A. P. TROTTER directed attention to an article by the inventor of the "Hatchet" in the current number of *Engineering*.

Dr. MACFARLANE GRAY said he had examined the proof given in *Engineering*, and found no error. He then showed how the Amsler planimeter could be explained in a simple geometrical manner by drawing radial lines through the pole and intersecting the curve. Moving the tracer along these radii added nothing to the area; motion along the arcs was the important component.

Mr. O. G. Jones and Prof. Thompson also took part in the discussion.

Mr. F. W. HILL made a communication on "*The Hatchet Planimeter*."

In this paper the author takes a point within the area to be measured and divides the area into elementary triangles with this point as apex. The tracing point of the planimeter is then supposed to start from the apex and trace out one of the triangles. The inclination between the initial and final positions of the hatchet is then expressed in terms of the angle at the apex, the radius vector, and the length of the planimeter. By expanding and integrating the expression, it is shown that twice the area between the initial and final position of the planimeter after tracing all the triangles is represented by an infinite series of terms, the first of which is the area of the curve, the second is proportional to the moment of inertia of the area about the point, the third proportional to its first moment about the same point. The higher terms are usually small enough to be neglected. Starting the tracer at the centroid of the area causes the third term to disappear, and the second has its minimum value, so that this is the starting point recommended. The magnitude of the errors caused by neglecting the various terms are discussed in some detail. In the author's opinion, the instrument can never be strictly accurate, but usually the errors are within the limits of observation.

Prof. HENRICI did not agree with the statement that the instrument was necessarily inaccurate, and thought geometry might aid analysis to find the proper starting point. For a symmetrical curve he had shown that a point existed, starting from which the area traced by the hatchet end was zero.

Dr. MACFARLANE GRAY thought Prof. Henrici's latter argument was vitiated by his figures not being correctly drawn; but this Prof. Henrici disputed.

Mr. O. G. JONES said Prof. Henrici's construction was not obvious, for the cusp curves traced by the hatchet end depended on the starting point.

Mr. YULE suggested that by shortening the planimeter it might be possible to bring the third and second terms of Mr. Hill's formula into greater prominence, and by going round the curve more than once determine the first and second moments.

A paper on "*A New Integrating Apparatus*," by Mr. A. SHARP, B.Sc., was taken as read.

The paper describes an improved form of harmonic analyser, giving the amplitude and epoch of each constituent term, the mechanism of which is an inversion of that described in a communication made to the Society on April 13th. Numerous drawings accompany the paper, showing the various parts in detail. The mechanism is also shown to be applicable for integraphs, and by suitable modification may be employed for mechanically integrating differential equations of various forms.

A paper on "*Magnetic Shielding by a Hollow Cylinder*," by Prof. PERRY, and another on "*Clark's Cells*," by Mr. S. SKINNER, were postponed.

Before adjourning, the Chairman announced that in future the meetings would be held in the rooms of the Chemical Society, Burlington House.

NOTICES OF BOOKS.

Eighteenth Annual Report of Her Majesty's Inspectors of Explosives; being their Annual Report for the year 1893. London: Eyre and Spottiswoode.

AFTER being one of Her Majesty's Inspectors of Explosives for upwards of ten years, Lieut.-Col. Cundill has at length been obliged to retire, owing to ill health; during this period he has made a name in connection with explosives which will long be remembered, and much regret has been expressed at his enforced retirement.

The only modification here mentioned of the existing law with regard to explosives that has been made during the year, is one which authorises the packing of explosives of the first division of the third (nitro-compound) class, in packages constructed of metal. The object of this order was to put manufacturers of smokeless powder, of which nitro-glycerin is an ingredient, on equal terms with those whose powder consisted essentially of nitro-cellulose.

There is a decrease of two in the number of factories since last year, the number standing now at 127, but it may be noted that there are at present eight applications under consideration: all of these factories have been visited at least once during the year, and more than half of them twice, and we are happy to observe that irregularities in the factories are now of rare occurrence.

With regard to the dangerous practice of manufacturing fireworks in private houses, for use "at a Carnival held annually about the 5th of November," the Inspectors express the hope that this practice is dying out, as fireworks can be legally obtained so easily. We find that the number of magazines has decreased from 382 to 381, and fortunately there has been no accident by fire or explosion in any magazine during the year.

We are glad to see that there has been a large decrease in the quantity of nitro-glycerin compounds imported during the year; and as the number of detonators imported has greatly increased, it shows that—though the detonator trade is still largely in the hands of foreign competitors—the home manufacture of dynamite and blasting gelatin is greatly on the increase.

Five new samples of smokeless powder have been submitted to the chemical adviser of the department, of which two have been reported on, and three are still under examination.

The number of accidents by fire or explosion which have come before the notice of the department this year was 113, causing 32 deaths and injuring 104 persons. This is a large decrease in the number of accidents, but an increase of two over last year in the number of deaths; but if these figures be compared with the average of the last ten years, it will be seen that the general improvement is very satisfactory. We may here remark that the Government Factory at Waltham Abbey, which has lately been the scene of several unfortunate explosions, does

public laboratory which is to give the devotees of pure science, anxious and willing to follow in the footsteps of the illustrious men who have built up the proud edifice of modern science, the facilities necessary for research in chemistry, and more particularly in that branch of the science called physical chemistry.

"I have come to the same conclusion as the promoters of the scheme of 1843, viz., that such laboratory would still have the greatest prospect of success under the ægis of the Royal Institution, that in fact it would be the consummation of the work which this great Institution has been fostering in its own laboratory, with such remarkable results, by the aid of the eminent men whose services it has always been fortunate enough to procure.

"As only want of space prevented the Royal Institution undertaking this task fifty years ago, I took the opportunity which offered itself last year of acquiring the premises, No. 20, Albemarle Street, adjoining the Institution. This property I found very suitable for the purpose of such a laboratory, and large enough to afford, besides, facilities to the Royal Institution for a much needed enlargement of its present laboratory and its libraries and reception rooms, which I should with great pleasure put at the disposal of the Institution.

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Prof. W. E. AYRTON, F.R.S., Past Presi[dent].

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...luminium upon Carbon and its Com-... Franck.—The author discusses the action ...pon carbonic acid, upon carbon monoxide, ...nates, and upon carbon. He finds it proved ...m enters into a definite combination with ... he hopes to succeed in isolating.

...tion.—Oechsher de Coninck.—The correction ...ee papers which the author had presented to ...my of Sciences, and which appeared in the ...le la Société Chimique* on July 5th, 1893.

... New Barometer for the Laboratory.—L. ...me. — The object of this instrument is to obviate ...xpedite the corrections necessary for other types of ...eters. The construction of the apparatus is not ...wn.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Bricks.—Is any process at present in use by which bricks to stand a pressure of 50 tons to the square inch can be made to take the requisite consistency (*i.e.*, to set sufficiently hard), by mixing a suitable chemical admixture with the materials, and so dispensing with kiln burning? Has such a method of making bricks ever been tried on a commercial scale with success? In that case what materials and chemical admixture have been employed?—T. VEASEY.

Established] **H. K. LEWIS,** [1844.

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not (or did not) come under the cognisance of Her Majesty's Inspectors.

A number of explosions are described, both at home and abroad, among them being the terrible disaster at Santander on the 3rd of November last, when about 33 tons of dynamite blew up, almost wrecking the town, and causing the death of 510 persons, and injuries to about 2000 more.

Proceedings of the American Pharmaceutical Association, at the Forty-first Annual Meeting, held at Chicago, August, 1893. Philadelphia: published by the American Pharmaceutical Association.

An unavoidable delay of about two months in the issue of this volume has been caused by the lamented death of the Permanent Secretary, Prof. John M. Maisch, in September last, of whom an obituary notice, with portrait, holds a prominent position in this number. The programme for the meeting, which extended over ten days, includes, as is usual on such occasions, a certain number of formal sittings for the reading and discussion of numerous papers, agreeably varied by visits to the exhibition, receptions, and other social functions. The papers read cover a wide field, due prominence being given to commercial interest and education, as well as to purely scientific subjects and research. A noteworthy feature of the volume is the excellent index, filling thirty pages of small type.

Everybody's Pocket Cyclopædia. By Don Lemon. Special Edition. For the London and Universal Bank, Ld., 449, Strand, S.W. 630th Thousand.

A previous edition of this little Cyclopædia was noticed in these columns some time ago (vol. lxvi., p. 148). It appears to be in all respects the same as the one then published by Saxon and Co. It is evidently widely appreciated, inasmuch as 120 thousands have meanwhile been issued.

CORRESPONDENCE.

SOLUTION AND DISSOLUTION.

To the Editor of the Chemical News.

Sir,—The term *solution* is used by chemists in two different senses; firstly, in the sense that a dissolved substance can be recovered unchanged by suitable means; and secondly, in the sense that the substance dissolved is decomposed, and is irrecoverable in its original condition by the ordinary methods. As the indiscriminate use of this word and its derivatives (soluble, dissoluble, &c.) tends to some confusion—at any rate in the minds of most students—I would suggest that the term *solution* and its corresponding derivatives be applied solely to the action taking place in the first case, while the word *dissolution* and verb *dissolutes* be used to describe the action in the second case. For example, we might say—Urea is soluble in water, but dissolutes in concentrated sulphuric acid. I am aware that the words "soluble with decomposition" are frequently used to express the second case; but the use of a single word to convey the same meaning would, I think, be fraught with some advantages. I know, also, that "dissociation" and "dissociates" could be used in the place of the words suggested; but they seem so exclusively employed by chemists to signify the decomposition of gaseous compounds by heat, that it would be perhaps best to retain them for that purpose only.—I am, &c.,

H. Smith Webster.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxviii., No. 25, June 18, 1894.

The Principle of Maximum Work and of Entropism.—M. Berthelot.—This voluminous paper, which commences with a controversial reference to the work of Dr. Thomsen, especially directed against the notion of the avidity of acids, and against the "equivocal term, thermic tonality," does not admit of useful abstraction.

Detection of Traces of Chlorine.—A. Villiers and M. Fayolle.—This paper will be inserted in full.

On the Emetics.—E. Maumené.—The author describes the "emetics" of silver, sodium, potassium (the ordinary tartar emetic), and lead. He concludes that in an acid, a salt, or in any compound whatever, water never plays a twofold part—water of combination, water of crystallisation; it is united in a single mass to the anhydrous substance in the proportions of the general law:—$\frac{1}{4}$, $\frac{2}{7}$, $\frac{3}{10}$, $\frac{4}{13}$, $\frac{1}{5}$, $\frac{2}{9}$, $\frac{3}{13}$ . . . . $\frac{1}{4}$, ... or, inversely, as $\frac{1}{4}$, $\frac{2}{7}$. . . . It escapes at higher or lower temperatures according to these proportions. An anhydrous acid is that from which the maximum of water has been separated without causing it to lose its essential character. The remark of Berzelius of a constant relation between the oxygen of the bases is not exact, and cannot be admitted. With O 8·23 in the acid of the emetics, we may find O 0·92 in the salt of lithium, and O 4·037 in the ordinary potassium emetic. The composition of all bodies, without the slightest exception, is subject to the general law of the actions of mixture, and of no other.

Influence of Fluorine upon Beer Yeasts.—J. Effront.—The author has previously shown that by cultivating beer yeasts in a medium containing fluorine compounds, they finally become accustomed to these antiseptics, so that their cellules are able to resist doses of fluorine which cellules not so acclimatised could not support. This acclimatisation notably modifies the chemical work of the cellules. The increase of the alcohol, the decrease of the production of glycerin and succinic acid, must be ascribed to the different behaviour of the yeasts according as they have, or have not, been accustomed to the compounds of fluorine.

Bulletin de la Société Chimique de Paris. Series 3, Vols. xi.-xii., No. 8.

Trehalose of Mushrooms, with reference to a Paper by Winterstein.—Em. Bourquelot.—Winterstein declared that during the desiccation of mushrooms, or even on keeping the recent heads, the trehalose, if present, totally disappears. Bourquelot shows in reply that three species retain trehalose after desiccation.

Reply to A. Combes.—L. Bouveault.—A controversial paper on stereo-chemistry, in which the author pronounces his opponent as lacking both amenity and authority.

Some Secondary Allylic Alcohols.—H. Fournier.—In this series of alcohols, as well as in that of their acetic ethers, the index of refraction increases by 0·003 for each term. The index of refraction of an acetic ether is exactly 0·012 less than that of the alcohol from which it is derived.

Hydration of Acetylene; Formation of Paraldehyd.—A. Desgrez.—The author has obtained in the distillation of the product submitted to the action of water at an elevated temperature a liquid with a well-marked aldehydic function. The boiling-point of this substance is

higher than 40°. It reduces silver oxide, yielding silver acetate. Only two substances possess these properties: paraldehyd and metaldehyd. As the compound is soluble in water, the author concludes that it consists of paraldehyd. Hence the direct hydration of acetylene gives rise to ethylic aldehyd, which is transformed into paraldehyd by the normal condensation of three molecules.

Some Tartaric Ethers with Secondary Chains.—M. Freundler.—A lengthy paper not adapted for useful abstraction.

No. 9.

E. Maumené called attention to his general law which renders it possible to calculate beforehand the yield of a reaction. He affirmed that this law alone (excepting the law of contact) enables us to solve with entire certainty the general chemical problem: to study entire chemical actions. At the next meeting the same chemist maintained that there was nothing certain in chemistry except, 1st, the equivalents or atoms, and, 2nd, his two laws.

Action of Sulphuric Acid upon Charcoal. — M. Giraud.—The author concludes from his experiments that no pyromellic acid is produced when sulphuric acid is caused to act upon wood charcoal which has been ignited to white redness, or upon coke. Hence he concludes that pyromellic acid is formed at the expense of a hydrogenous or oxygenous matter remaining in ordinary charcoal.

Hydration of Allylene, $CH_3—C\equiv CH$ (Methylacetylenepropine).—A. Dasgrez. The fixation of the elements of water upon allylene takes place according to the formula $CH_3—C\equiv CH + H_2O = CH_3—CO—CH_3$, since the compound obtained possesses none of the reductive properties of the aldehyds.

On Campholene.—M. Guerbat.—Campholene is a colourless liquid, of an odour analogous to that of turpentine, and a burning taste. It boils at 134° under the pressure of 758 m.m. In the liquid state its specific gravity is 0·8115. It is without rotatory power. It is insoluble in water, but soluble in alcohol, and mixes with ether, chloroform, and carbon disulphide. The author has studied its behaviour with bromine, gaseous hydriodic acid, a mixture of fuming nitric and sulphuric acids, with bromine in presence of aluminium bromide.

On the Blue Colouration assumed by Leuco-Auramine in contact with Acids.—A. Rosenstiehl.—The notion of a blue modification of leuco-auramine must be abandoned. The substance which Graebe considers as such is the diamidic and tetramethylated benzhydrol,—

$$A_2 = C{<}^{OH}_{H}$$

the chlorohydrine of which possesses a rich blue colour.

Oil of Ylang-ylang. — A. Reychler.—The author assigns to the portion which passes over on re-distillation the formula $C_{10}H_{18}O$. Hence it belongs to the alcohols of which the type is geraniol. The boiling-point of ylangol at a pressure of 28 m.m. is from 103° to 108°. Its molecular weight is 150, theory demanding 154. Its specific gravity as a liquid is 0·886 at 15°. The index of refraction at 15·5° and for the yellow sodium light is 1·47165, and its molecular refractive power is = 48·64. The rotatory power is $[\alpha]_D = -20·7$.

Formation of Mannite in Wines.—H. and A. Malbot.—After having effected a rapid and complete fermentation of the must, the formation of mannite may be prevented, if required, by energetic sulphuring.

No. 10.

Reclamation on the Subject of Pseudo-pelletierine.—C. Tanret.—The author protests against the use of the name *granatonine* instead of *pseudo-pelletierine*, as proposed by Ciamician and Silber.

Atomic Weight of Thallium.—Charles Lepierre.—The author upholds the value 203·62.

On a Singular Case of Metallic Precipitation.—J. B. Senderens.—It results from the author's experiments that, at ordinary temperatures, lead precipitates lead from the neutral solutions of its nitrate, exactly as would do a plate of iron or of zinc. The same result is obtained if the lead employed is chemically pure.

Preparation of Campholic Acid. — M. Guerbet.—This memoir is too long for useful abstraction.

Determination of Nitric Acid in Waters in the State of Nitrogen Binoxide.—A. Barille.—This paper will be inserted in full.

On certain Points of Stereo-Chemistry: a Reply to M. Bouveault.—A. Combes.—The author, in concluding this controversy, emphasises the impossibility of admitting that the four valencies of carbon could act in a plane, this being one of the fundamental principles of stereo-chemical reasoning.

Action of Aluminium upon Carbon and its Compounds.—Léon Franck.—The author discusses the action of aluminium upon carbonic acid, upon carbon monoxide, upon the carbonates, and upon carbon. He finds it proved that aluminium enters into a definite combination with carbon, which he hopes to succeed in isolating.

A Correction.—Oechsher de Coninck.—The correction refers to three papers which the author had presented to the Academy of Sciences, and which appeared in the *Bulletin de la Société Chimique* on July 5th, 1893.

On a New Barometer for the Laboratory.—L. Maquenne. — The object of this instrument is to obviate or to expedite the corrections necessary for other types of barometers. The construction of the apparatus is not shown.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

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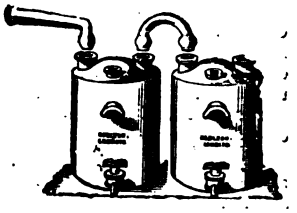

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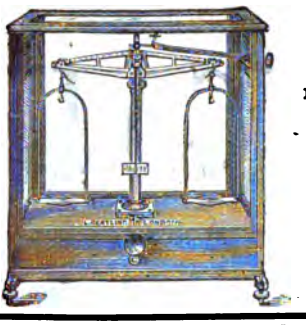

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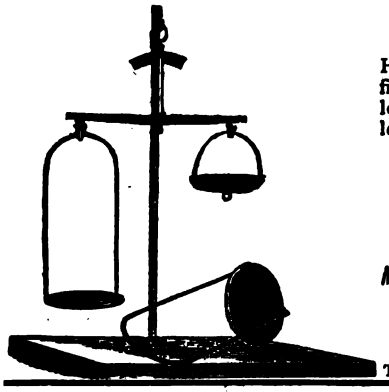

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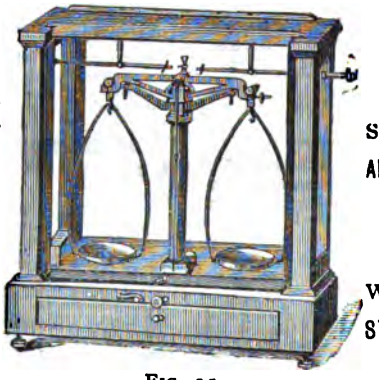

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THE CHEMICAL NEWS.

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FLAME SPECTRA AT HIGH TEMPERATURES.*

By W. N. HARTLEY, F.R.S.

(Concluded from p. 3).

Part III.—The Spectroscopic Phenomena and Thermo-Chemistry of the Bessemer Process.

The flame issuing from the mouth of a Bessemer converter was first investigated by Sir Henry Roscoe (*Literary and Phil. Soc., Manchester, Proc.*, iii., p. 57; and *Phil. Mag.*, xxxiv., p. 437), in 1863; by Lielegg (*Sitzungsberichte Kaiserl. Akademie der Wissenschaften*, Wien, lvi., Part II.), and by Marshall Watts (*Phil. Mag.*, xxxiv., p. 437), in 1867; by Tunner (*Dingler's Polytech. Journ.*, clxxviii., p. 465), J. M. Silliman, Rowan (*Phil. Mag.*, xli., p. 1), Von Lichtenfels (*Dingler's Polytech. J.*, cxci., p. 213), Spear Parker (Chem. News, xxiii., p. 25), Kupelwieser (*Oesterreichische Zeitschr. für Berg- und Hütten-Wesen*, No. 8., p. 59, 1868), Brunner (*loc. cit.*, No. 29, p. 227, 1868), and Wedding (*Zeitschrift für das Berg- Hütten- und Salinen-Wesen*, xxvii., p. 117, 1869), in 1868; also by A. Greiner (*Revue Universelle*, xxxv., p. 623), in 1874.

Up to the present time the precise nature of the spectrum, the cause of its production, its sudden disappearance when decarburisation of the metal takes place, and the connection between the decarburisation of the metal and the extinction of the spectrum, have not been satisfactorily explained. According to Roscoe, Lielegg, Kupelwieser, and Spear Parker, the spectrum is characterised by bands of carbon or of carbon monoxide, which disappear when all carbon is burnt out of the metal.

On the other hand, the investigations of Simmler (*Zeit. fur Analytische Chemie*, 1862), Brunner, Von Lichtenfels, and Wedding, the spectrum is not due to carbon (Roscoe) or to carbon monoxide (Lielegg and Kupelwieser), but to manganese and other elements in the pig-iron.

The very careful examination of these spectra by Watts and his comparison of them with that of the Bessemer flame led to the conclusion that it was not the spectrum of carbon in any form nor of manganese, but that of manganic oxide. Lielegg established the fact that carbon monoxide yields a continuous spectrum, and that this gas causes the continuous bright spectrum of the Bessemer flame; but he also attributed certain lines or bands to the high temperature of the carbon monoxide. All observers are agreed as to the appearance after a certain interval of the lines of the alkali metals which were originally discovered by Roscoe to be present during the first period of the "blow." Watts observed the C line of hydrogen during wet weather.

This research was undertaken in 1882, and an instrument was devised for the purpose of photographing the spectra of various flames emitted during metallurgical operations. The work was left in abeyance until certain practical difficulties encountered in studying flame spectra at high temperatures in the laboratory had been overcome. The original mounting of the instrument was too light, but that which has recently been used with success is described.

Owing to the courtesy of Mr. T. W. Webb, the engineer of the Locomotive Department of the London and North Western Railway, and of Mr. E. P. Martin, the manager of the Dowlais Ironworks, observations have been made at Crewe and at Dowlais during the past year. About ninety spectra were photographed, about fifty of which were available for study.

The spectra studied extended from the red potassium line λ 7697, and on some of the plates to about the line P on Cornu's map of the solar spectrum, λ 3380·8; but the least refrangible line photographed was that of lithium, λ 6707. The bands and lines in various spectra taken at Crewe and Dowlais have been measured, and their wave-lengths determined. Descriptions of the spectra and how they were obtained are given. The description of each band and line measured is given, with its wave-length, its origin, and other references. Photographs of the spectra are presented, and a map has been drawn for the identification of the lines on these photographs. About ninety-two lines were identified with lines in the solar spectrum, with lines in Kayser and Runge's map of the arc spectrum of iron, and on spectra from steel and ferric oxide heated in the oxyhydrogen flame.

The Constitution of the Bessemer Spectrum.

The spectrum is a complex one which exhibits differences in constitution during different periods of the "blow," and even during different intervals in the same period. As originally observed by Watts, the spectrum differs in different works, the difference being due to temperature and to the composition of the metal blown.

During the First Period.—The lines of the alkali metals, sodium, potassium, and lithium, are seen unreversed on a bright continuous spectrum caused by carbon monoxide. The C line of hydrogen, and apparently the F line, were seen reversed during a snowstorm.

During the Second Period. The "Boil."—Bands of manganese are prominent, overlying the continuous spectrum of carbon monoxide. There are lines of carbon monoxide, manganese, and iron, also those of the alkali metals.

During the Third Period. The "Fining Stage."—The spectrum is the same as the foregoing, but the lines of iron are not so strong and not quite so well defined. Some of the short lines disappear. The lines of the alkali metals are visible.

It is also probable that some of the bands of manganese oxide are present, but they are obscured by the continuous carbon monoxide spectrum. No absorption bands were seen, no nitrogen bands, nor bands of calcium and magnesium oxide, neither did the lines of these metals appear. There is no trace of cobalt, nickel, chromium, or copper; certain carbon bands overlie those of manganese, and are recognised by measurements of their edges. Some of the lines not identified by Watts prove to be iron lines, others belong to manganese. The manganese bands are all degraded towards the red, the carbon bands towards the blue.

The Cause of the Non-appearance of Lines at the Commencement and Termination of the "Blow."

Some controversy followed upon the publication of the papers by Roscoe and Lielegg. Tunner stated that in Sweden the Bessemer process was not facilitated by the use of the spectroscope. Brunner pointed out that the spectroscopic phenomena were not dependent on the combustion of carbon, but were characteristic of the various impurities in the metal. Wedding and Silliman discussed the origin of the spectrum seen at different periods of the "blow," and failed to account fully at that time for the non-appearance of lines at its commencement and termination. Their views did not harmonise. Many facts were discovered which were not understood, appeared contradictory, and required verification. These have all been carefully examined and accounted for.

Support is given to Wedding's view, based on the analyses of Brunner, that the non-appearance of the lines of manganese at the commencement and termination of the blow is owing to the quantity of metal volatilised at those

* A Paper read before the Royal Society, June 14, 1894.

periods being insufficient for the production of a spectrum. At the commencement the temperature is too low, being very little above that of the molten metal; and, as free oxygen escapes along with carbon dioxide, the gaseous mixture contains too small a proportion of carbon monoxide. The alkalis which come from the ganister lining of the converter are present as silicates, and in very small proportion; many silicates, such as, for instance, felspar, do not exhibit spectra of the alkalis they contain until heated in the oxyhydrogen flame, but at this temperature the metals potassium, lithium, and rubidium have been detected with the greatest ease in such silicates. Similarly, the alkali metals do not show themselves in the Bessemer flame until a layer of slag has been formed, and the temperature has risen sufficiently high for these basic constituents to be vapourised. At the temperature of the "boil," or second period, both metallic manganese and iron are freely vapourised in a current of carbon monoxide, which, in a highly heated state, rushes out of the bath of molten metal. The evidence of this is the large number of bands of manganese and lines of iron in the spectrum.

When the metal blown contains but little manganese, as, for instance, hæmatite pig, this is all converted into silica during the first period. The manganese spectrum in the flame does not arise from that substance being contained in the bath of metal, it must be vapourised from the slag. That this is so has been proved by photographs of the spectrum from samples of slag obtained from the Crewe works. There is very little difference between these and the photographs of the flame-spectrum taken at Crewe, during the "boil," the difference being chiefly in the iron lines being stronger in the slag spectrum. This explains the fact observed by Brunner, namely, that when a converter is being heated with coke after it has been used, but not re-lined, the spectrum of the Bessemer flame makes its appearance; manifestly it comes from the adhering slag.

The luminosity of the flame during the "boil" is due, not merely to the combustion of highly heated carbonic oxide, but also to the presence of the vapours of iron and manganese in the gas.

The disappearance of the manganese spectrum at the end of the "fining stage," or third period, is primarily due to a reduction in the quantity of heated carbon monoxide escaping from the converter, which arises from the diminished quantity of carbon in the metal. When the last traces of carbon are gone, so that air may escape through the metal, the blast instantly oxidises any manganese, either in the metal or in the atmosphere of the converter, and, furthermore, oxidises some of the iron. The temperature must then fall with great rapidity.

The entire spectroscopic phenomena of the "blow" are undoubtedly determined by the chemical composition of the molten iron, and of the gases and metallic vapours within the converter, the temperature of the metal and that of the issuing gases.

The Temperature of the Bessemer Flame.

The probable temperature of the Bessemer flame at the finish is that produced by the combustion in cold air of carbonic oxide heated to about 1580° C.; that is to say, to the temperature which, according to Le Chatelier (*Comptes Rendus*, cxiv., p. 670), is that of the bath of molten metal from which the gas has proceeded. The bath of metal acts simultaneously as a means of heating the blast, producing the gas, and as a furnace, on the regenerative principle, which heats the gas prior to its combustion. The heating effect is therefore cumulative. The temperature, as is well known, can easily rise too rapidly, and the metal has then to be cooled by throwing cold pig-iron or even old ingot moulds into it.

If we may judge by the lines and bands belonging to iron and manganese which have been measured in photographed spectra of the Bessemer flame, the temperature must nearly approach that of the oxyhydrogen flame, and may easily attain the melting-point of platinum, namely, 1775° C. (Violle).

Marshall Watts observed (*Phil. Mag.*, 1870) that the sodium lines 5681 and 5687 may be employed as an index of temperature, since they are present in the spectrum of any flame containing sodium which is hot enough to melt platinum, but do not appear at lower temperatures. The Bessemer flame does not show this double line, but only the D lines.

We cannot, however, conclude from this that the flame is not hot enough to produce these lines, for though the temperature may be high enough, the quantity of material present is not sufficient to cause their appearance. Moreover, there are two intensely brilliant bands of manganese closely adjacent, one of which certainly overlies these lines. Lastly, they are not to be seen in the photographed spectrum obtained from slag heated in the oxyhydrogen flame, which melts platinum easily and slowly volatilises iridium wire.

From thermo-chemical data, the heat evolved during the "blow" has been calculated, but the specific heats of cast iron, slag, carbon monoxide, and nitrogen are unknown at temperatures between 1200° C. and 2000° C. If we allow for 50 per cent of the heat developed at high temperatures being lost by radiation or absorbed, then the estimated temperature of the metal in the converter is more than 1900° C.

Le Chatelier (*Comptes Rendus*, cxiv., p. 670) found the steel in the ladle of a Robert converter to be at 1640° C. Reasons are adduced for believing that it must certainly have been hotter than this at the highest temperature of the "blow."

The Technical Aspect of this Investigation.

The spectrum obtained from Bessemer slag by the oxyhydrogen flame is composed of precisely the most characteristic features of the flame spectrum, as seen issuing from the converter at Crewe. Hence at this temperature iron and manganese are freely volatilised, as they are in the oxyhydrogen flame. As a matter of course the continuous spectrum of carbon monoxide, the bands and lines of that compound, and of elementary carbon are absent from the slag spectrum. The flame spectrum at Dowlais differs from this, and resembles the spectrum of metallic manganese, or more closely that of ferro-manganese. For reasons given, I conclude that the spectrum at Crewe results from materials in the slag; but that at Dowlais from constituents vaporised from the bath of metal.

The complete termination of the "fining stage" is clearly indicated, but there is no indication by the flame of the composition of the metal within the converter at any previous stage. As the progress of the "blow" is governed by the composition of the metal and its temperature in the converter, and as these cannot be controlled with perfect exactitude during each "blow," it follows that the practice of complete decarburization* is the best course to pursue, the required amount of carbon and manganese being added subsequently in the forms of grey iron, spiegel, or ferro-manganese.

I propose to continue this work by extending my observations to the flame from the basic Bessemer process and the gases in the Siemens steel furnace.

German Association of Naturalists and Physicians.—This Congress, first established by the illustrious Lorenz Oken, will hold this year its sixty-sixth meeting at Vienna on September 24th to 30th. There will be be thirty sections. The dangerous subjects of Economy and Statistics are judiciously avoided, an example which the British Association still neglects to follow.

* The words "carburizing" and "decarburizing" are to be preferred to "carbonising and "decarbonising" when applied to metals, because these expressions were those originally used in the older works on metallurgy, and they avoid confusion with the other signification of the word "carbonising."

THE SCIENTIFIC WORK OF TYNDALL.*

By Lord RAYLEIGH, M.A., D.C.L., LL.D., F.R.S.,
Professor of Natural Philosophy, R.I.

IT is fitting that the present season should not pass without a reference on these evenings to the work of him whose tragic death a few months since was felt as a personal grief and loss by every member of the Royal Institution. With much diffidence I have undertaken the task to-night, wishing that it had fallen to one better qualified by long and intimate acquaintance to do justice to the theme. For Tyndall was a personality of exceeding interest. He exercised an often magical charm upon those with whom he was closely associated, but when his opposition was aroused he showed himself a keen controversialist. My subject of to-night is but half the story.

Even the strictest devotion of the time at my disposal to a survey of the scientific work of Tyndall will not allow of more than a very imperfect and fragmentary treatment. During his thirty years of labour within these walls he ranged over a vast field, and accumulated results of a very varied character, important not only to the cultivators of the physical sciences, but also to the biologist. All that I can hope to do is to bring back to your recollection the more salient points of his work, and to illustrate them where possible by experiments of his own devising.

In looking through the catalogue of scientific papers issued by the Royal Society, one of the first entries under the name of Tyndall relates to a matter comparatively simple, but still of some interest. It has been noticed that when a jet of liquid is allowed to play into a receiving vessel, a good deal of air is sometimes carried down with it, while at other times this does not happen. The matter was examined experimentally by Tyndall, and he found that it was closely connected with the peculiar transformation undergone by a jet of liquid which had been previously investigated by Savart. A jet as it issues from the nozzle is at first cylindrical, but after a time it becomes what the physiologists call *varicose*; it swells in some places and contracts in others. This effect becomes more exaggerated as the jet descends, until the swellings separate into distinct drops, which follow one another in single file. Savart showed that under the influence of vibration the resolution into drops takes place more rapidly, so that the place of resolution travels up closer to the nozzle.

Tyndall's observation was that the carrying down of air required a jet already resolved into drops when it strikes the liquid. I hope to be able to show you the experiment by projection upon the screen. At the present moment the jet is striking the water in the tank previous to resolution into drops, and is therefore carrying down no air. If I operate on the nozzle with a vibrating tuning-fork, the re-solution occurs earlier, and the drops now carry down with them a considerable quantity of air.

Among the earlier of Tyndall's papers are some relating to ice, a subject which attracted him much, probably from his mountaineering experiences. About the time of which I am speaking Faraday made interesting observations upon a peculiar behaviour of ice, afterwards called by the name of regelation. He found that if two pieces of ice were brought into contact they stuck or froze together. The pressure required to produce this effect need not be more than exceedingly small. Tyndall found that if fragments of ice are squeezed they pack themselves into a continuous mass. We have here some small ice in a mould, where it can be subjected to a powerful squeeze. The ice under this operation will be regelated, and a mass obtained which may appear almost transparent, and as if it had never been fractured at all. The flow of glaciers has been attributed to this action, the fractures which the stresses produce being mended again by regelation. I should say, perhaps, that the question of glacier motion presents difficulties not yet wholly explained. There can be no doubt, however, that regelation plays an important part.

Another question treated by Tyndall is the manner in which ice first begins to melt under the action of a beam of light passing into it from an electric lamp. Ice usually melts by conducted heat, which reaches first the outside layers. But if we employ a beam from an electric lamp, the heat will reach the ice not only outside but internally, and the melting will begin at certain points in the interior. Here we have a slab of ice which we project upon the screen. We see that the melting begins at certain points, which develop a crystallised appearance resembling flowers. They are points in the interior of the ice, not upon the surface. Tyndall found that when the ice gives way at these internal points there is a formation of apparently empty space. He carefully melted under water such a piece of ice, and found that when the cavity was melted out there was no escape of air, proving that the cavity was really vacuous.

Various speculations have been made as to the cause of this internal melting at definite points, but here again I am not sure if the difficulty has been altogether removed. One point of importance brought out by Tyndall relates to the plane of the flowers. It is parallel to the direction in which the ice originally froze, that is, parallel to the original surface of the water from which it was formed.

I must not dwell further upon isolated questions, however interesting; but will pass on at once to our main subject, which may be divided into three distinct parts, relating, namely, to heat, especially dark radiation, sound, and the behaviour of small particles, such as compose dust, whether of living or dead matter.

The earlier publications of Tyndall on the subject of heat are for the most part embodied in his work entitled "Heat as a Mode of Motion." This book has fascinated many readers. I could name more than one now distinguished physicists who drew their first scientific nutriment from it. At the time of its appearance the law of the equivalence of heat and work was quite recently established by the labours of Meyer and Joule, and had taken firm hold of the minds of scientific men; and a great part of Tyndall's book may be considered to be inspired by and founded upon this first law of thermodynamics. At the time of publication of Joule's labours, however, there seems to have been a considerable body of hostile opinion, favourable to the now obsolete notion that heat is a distinct entity called caloric. Looking back, it is a little difficult to find out who were responsible for this reception of the theory of caloric. Perhaps it was rather the popular writers of the time than the first scientific authorities. A scientific worker, especially if he devotes himself to original work, has not time to examine for himself all questions, even those relating to his own department, but must take something on trust from others whom he regards as authorities. One might say that a knowledge of science, like a knowledge of law, consists in knowing where to look for it. But even this kind of knowledge is not always easy to obtain. It is only by experience that one can find out who are most entitled to confidence. It is difficult now to understand the hesitation that was shown in fully accepting the doctrine that heat is a mode of motion, for all the great authorities, especially in England, seem to have favoured it. Not to mention Newton and Cavendish, we have Rumford making almost conclusive experiments in its support, Davy accepting it, and Young, who was hardly ever wrong, speaking of the antagonistic theory almost with contempt. On the Continent, perhaps, and especially among the French school of chemists and physicists, caloric had more influential support.

As has been said, a great part, thought not the whole, of Tyndall's work was devoted to the new doctrine. Much relates to other matters, such as radiant heat. Objection

* A Lecture delivered at the Royal Institution of Great Britain, March 16, 1894.

has been taken to this phrase, not altogether without reason; for it may be said that when heat it is not radiant, and while radiant it is not heat. The term dark radiation, or dark radiance as Newcombe calls it, is preferable, and was often used by Tyndall. If we analyse, as Newton did, the components of light, we find that only certain parts are visible. The invisible parts produce, however, as great, or greater, effects in other ways than do the visible parts. The heating effect, for example, is vastly greater in the invisible region than in the visible. One of the experiments that Tyndall devised in order to illustrate this fact, I hope now to repeat. He found that it was possible by means of a solution of iodine in bisulphide of carbon to isolate the invisible rays. This solution is opaque to light; even the sun could not be seen through it; but it is very fairly transparent to the invisible ultra-red radiation. By means of a concave reflector I concentrate the rays from an arc lamp. In their path is inserted the opaque solution, but in the focus of invisible radiation the heat developed is sufficient to cause the inflammation of a piece of gun-cotton.

Tyndall varied this beautiful experiment in many ways. By raising to incandescence a piece of platinum foil, he illustrated the transformation of invisible into visible radiation.

The most important work, however, that we owe to Tyndall in connection with heat is the investigation of the absorption by gaseous bodies of invisible radiation. Melloni had examined the behaviour of solid and liquid bodies, but not of gaseous. He found that transparent bodies, like glass, might be very opaque to invisible radiation. Thus, as we all know, a glass screen will keep off the heat of a fire, while if we wish to protect ourselves from the sun, the glass screen would be useless. On the other hand, rock salt freely transmitted invisible radiation. But nothing had been done on the subject of gaseous absorption, when Tyndall attacked this very difficult problem. Some of his results are shown in the accompanying table. The absorption of the ordinary non-condensable, or rather not easily condensable, gases—for we must not talk of non-condensable gases now, least of all in this place—the absorption of these gases is very small; but when we pass to the more compound gases, such as nitric oxide, we find the absorption much greater—and in the case of olefiant gas we see that the absorbing power is as much as 6000 times that of the ordinary gases.

	Relative absorption at 1 inch pressure.
Air	1
Oxygen	1
Nitrogen	1
Hydrogen	1
Carbonic acid	972
Nitric oxide	1590
Ammonia	5460
Olefiant gas	6030

There is one substance as to which there has been a great diversity of opinion—aqueous vapour. Tyndall found that aqueous vapour exercises a strong power of absorption—strong relatively to that of the air in which it is contained. This is, of course, a question of great importance, especially in relation to meteorology. Tyndall's conclusions were vehemently contested by many of the authorities of the time, among whom was Magnus, the celebrated physicist of Berlin. With a view a view to this lecture, I have gone somewhat carefully into this question, and I have been greatly impressed by the care and skill showed by Tyndall, even in his earlier experiments upon this subject. He was at once sanguine and sceptical—a combination necessary for success in any branch of science. The experimentalist who is not sceptical will be led away on a false tack and accept conclusions which he would find it necessary to reject were he to pursue the matter further; if not sanguine, he will be discouraged altogether by the difficulties encountered in his earlier efforts, and so arrive at no conclusion at all. One criticism, however, may be made. Tyndall did not at first describe with sufficient detail the method and the precautions which he used. There was a want of that precise information necessary to allow another to follow in his steps. Perhaps this may have been due to his literary instinct, which made him averse from overloading his pages with technical experimental details.

The controversy above referred to I think we may now consider to be closed. Nobody now doubts the absorbing power of aqueous vapour. Indeed, the question seems to have entered upon a new phase; for in a recent number of *Wiedemann's Annalen*, Paschen investigates the precise position in the spectrum of the rays which are absorbed by aqueous vapour.

I cannot attempt to show you here any of the early experiments on the absorption of vapours. But some years later Tyndall contrived an experiment which will allow of reproduction. It is founded on some observations of Graham Bell, who discovered that various bodies became sonorous when exposed to intermittent radiation.

The radiation is supplied from incandescent lime, and is focussed by a concave reflector. In the path of the rays is a revolving wheel provided with projecting teeth. When a tooth intervenes, the radiation is stopped; but in the interval between the teeth the radiation passes through, and falls upon any object held at the focus. The object in this case is a small glass bulb containing a few drops of ether, and communicating with the ear by a rubber tube. Under the operation of the intermittent radiation the ether vapour expands and contracts; in other words, a vibration is established, and a sound is heard by the observer. But if the vapour were absolutely diathermanous, no sound would be heard.

I have repeated the experiment of Tyndall which allowed him to distinguish between the behaviour of ordinary air and dry air. If, dispensing with ether, we fill the bulb with air in the ordinary moist state, a sound is heard with perfect distinctness, but if we drop in a little sulphuric acid, so as to dry the air, the sound disappears.

According to the law of exchanges, absorption is connected with radiation; so that while hydrogen or oxygen do not radiate, from ammonia we might expect to get considerable radiation. In the following experiment I aim at showing that the radiation of hot coal-gas exceeds the radiation of equally hot air.

The face of the thermopile, protected by screens from the ball itself, is exposed to the radiation from the heated air which rises from a hot copper ball. The effect is manifested by the light reflected from a galvanometer mirror. When we replace the air by a stream of coal-gas, the galvanometer indicates an augmentation of heat, so that we have before us a demonstration that coal-gas when heated does radiate more than equally hot air, from which we conclude that it would exercise more absorption than air.

I come now to the second division of my subject, that relating to Sound. Tyndall, as you know, wrote a book on Sound, founded on lectures delivered in this place. Many interesting and original discoveries are there embodied. One that I have been especially interested in myself, is on the subject of sensitive flames. Professor Leconte in America made the first observations at an amateur concert, but it was Tyndall who introduced the remarkable high-pressure flame now before you. It issues from a pin-hole burner, and the sensitiveness is entirely a question of the pressure at which the gas is supplied. Tyndall describes the phenomenon by saying that the flame under the influence of a high pressure is like something on the edge of a precipice. If left alone, it will maintain itself; but under the slightest touch it will be pushed over. The gas at high pressure will, if undisturbed, burn steadily and erect, but if a hiss is made in its neighbourhood it becomes at once unsteady, and ducks down. A very high sound is necessary. Even a whistle,

as you see, does not act. Smooth pure sounds are practically without effect unless of very high pitch.

I will illustrate the importance of the flame as a means of investigation by an experiment in the diffraction of sound. I have here a source of sound, but of pitch so high as to be inaudible. The waves impinge perpendicularly upon a circular disc of plate glass. Behind the disc there is a sound shadow, and you might expect that the shadow would be most complete at the centre. But this is not so. When the burner occupies this position the flame flares; but when, by a slight motion of the disc, the position of the flame is made eccentric, the existence of the shadow is manifested by the recovery of the flame. At the centre the intensity of sound is the same as if no obstacle were interposed.

The optical analogue of the above experiment was made at the suggestion of Poisson, who had deduced the result theoretically, but considered it so unlikely that he regarded it as an objection to the undulatory theory of light. Now, I need hardly say, it is regarded as a beautiful confirmation.

It is of importance to prove that the flame is not of the essence of the matter, that there is no need to have a flame, or to ignite it at the burner. Thus, it is quite possible to have a jet of gas so arranged that ignition does not occur until the jet has lost its sensitiveness. The sensitive part is that quite close to the nozzle, and the flame is only an indicator. But it is not necessary to have any kind of flame at all. Tyndall made observations on smoke-jets, showing that a jet of air can be made sensitive to sound. The difficulty is to see it, and to operate successfully upon it; because, as Tyndall soon found, a smoke-jet is much more difficult to deal with than flames, and is sensitive to much graver sounds. I doubt whether I am wise in trying to exhibit smoke-jets to an audience, but I have a special means of projection by which I ought at least to succeed in making them visible. It consists in a device by which the main part of the light from the lamp is stopped at the image of the arc, so that the only light which can reach the screen is light which by diffusion has been diverted out of its course. Thus we shall get an exhibition of a jet of smoke upon the screen, showing bright on a dark ground. The jet issues near the mouth of a resonator of pitch 256. When undisturbed it pursues a straight course, and remains cylindrical. But if a fork of suitable pitch be sounded in the neighbourhood, the jet spreads out into a sort of fan, or even bifurcates, as you see upon the screen. The real motion of the jet cannot of course be ascertained by mere inspection. It consists in a continuously increasing *sinuosity*, leading after a while to complete disruption. If two forks slightly out of unison are sounded together, the jet expands and re-collects itself, synchronously with the audible beats. I should say that my jet is a very coarse imitation of Tyndall's. The nozzle that I am using is much too large. With a proper nozzle, and in a perfectly undisturbed atmosphere,—undisturbed not only by sounds, but free from all draughts,—the sensitiveness is wonderful. The slightest noise is seen to act instantly, and to bring the jet down to a fraction of its former height.

Another important part of Tyndall's work on Sound was carried out as adviser of the Trinity House. When in thick weather the ordinary lights fail, an attempt is made to replace them with sound signals. These are found to vary much in their action, sometimes being heard to a very great distance, and at other times failing to make themselves audible even at a moderate distance. Two explanations have been suggested, depending upon acoustic refraction and acoustic reflection.

Under the influence of variations of temperature refraction occurs in the atmosphere. For example, sound travels more quickly in warm than in cold air. If, as often happens, it is colder above, the upper part of the sound-wave tends to lag behind, and the wave is liable to be tilted upwards, and so to be carried over the head of the would-be observer on the surface of the ground. This explanation of acoustic refraction by variation of temperature was given by Prof. Osborne Reynolds. As Sir G. Stokes showed, refraction is also caused by wind. The difference between refraction by wind and by temperature variations is that in one case everything turns upon the direction in which the sound is going, while in the second case this consideration is immaterial. The sound is heard by an observer down wind, and not so well by an observer up wind. The explanation by refraction of the frequent failure of sound signals was that adopted by Prof. Henry in America, a distinguished worker upon this subject. Tyndall's investigations, however, led him to favour another explanation. His view was that sound was actually reflected by atmospheric irregularities. He observed, what appears to be amply sufficient to establish his case, that prolonged signals from fog sirens give rise to echoes audible after the signal has stopped. This echo was heard from the air over the sea, and lasted in many cases a long time, up to fifteen seconds. There seems here no alternative but to suppose that reflection must have occurred internally in the atmosphere. In some cases the explanation of the occasional diminished penetration of sound seems to be rather by refraction, and in others by reflection.

Tyndall proved that a single layer of hot air is sufficient to cause reflection, and I propose to repeat his experiment. The source of sound, a toy reed, is placed at one end of one metallic tube, and a sensitive flame at one end of a second. The opposite ends of these tubes are placed near each other, but in a position which does not permit the sound-waves issuing from the one to enter the other directly. Accordingly the flame shows no response. If, however, a pane of glass be held suitably, the waves are reflected back and the flame is excited. Tyndall's experiment consists in the demonstration that a flat gas-flame is competent to act the part of a reflector. When I hold the gas-flame in the proper position, the percipient flame flares; when the flat flame is removed or held at an unsuitable angle, there is almost complete recovery.

It is true that in the atmosphere no such violent transitions of density can occur as are met with in a flame; but, on the other hand, the interruptions may be very numerous, as is indeed rendered probable by the phenomena of stellar scintillation.

The third portion of my subject must be treated very briefly. The guiding idea of much of Tyndall's work on atmospheric particles was the application of an intense illumination to render them evident. Fine particles of mastic, precipitated on admixture of varnish with a large quantity of water, had already been examined by Brücke. Chemically precipitated sulphur is convenient, and allows the influence of size to be watched as the particles grow. But the most interesting observations of Tyndall relate to precipitates in gases caused by the chemical action of the light itself. This may be illustrated by causing the concentrated rays of the electric lamp to pass through a flask containing vapour of peroxide of chlorine. Within a few seconds dense clouds are produced.

When the particles are very small in comparison with the wave-length, the laws governing the dispersion of the light are simple. Tyndall pursued the investigation to the case where the particles have grown beyond the limit above indicated, and found that the polarisation of the dispersed light was effected in a peculiar and interesting manner.

Atmospheric dust, especially in London, is largely organic. If, following Tyndall, we hold a spirit-lamp under the track of the light from the electric lamp, the dark spaces, resulting from the combustion of the dust, have all the appearance of smoke.

In confined and undisturbed spaces the dust settles out. I have here a large flask which has been closed for some days. If I hold it to the lamp, the track of the light,

plainly visible before entering and after leaving the flask, is there interrupted. This, it will be evident, is a matter of considerable importance in connection with organic germs.

The question of the spontaneous generation of life occupied Tyndall for several years. He brought to bear upon it untiring perseverance and refined experimental skill, and his results are those now generally accepted. Guarding himself from too absolute statements as to other times and other conditions, he concluded that under the circumstances of our experiments life is always founded upon life. The putrefaction of vegetable and animal infusions, even when initially sterilised, is to be attributed to the intrusion of organic germs from the atmosphere.

The universal presence of such germs is often regarded as a hypothesis difficult of acceptance. It may be illustrated by an experiment from the inorganic world. I have here, and can project upon the screen, glass pots, each containing a shallow layer of a supersaturated solution of sulphate of soda. Protected by glass covers, they have stood without crystallising for forty-eight hours. But if I remove the cover, a few seconds or minutes will see the crystallisation commence. It has begun, and long needles are invading the field of view. Here it must be understood that, with a few exceptions, the crystalline germ required to start the action must be of the same nature as the dissolved salt; and the conclusion is that small crystals of sulphate of soda are universally present in the atmosphere.

I have now completed my task. With more or less success I have laid before you the substance of some of Tyndall's contributions to knowledge. What I could not hope to recall was the brilliant and often poetic exposition by which his vivid imagination illumined the dry facts of science. Some reminiscence of this may still be recovered by the reader of his treatises and memoirs; but much survives only as an influence exerted upon the minds of his contemporaries, and manifested in subsequent advances due to his inspiration.

PROVISIONAL METHODS OF CHEESE ANALYSIS.*

Sampling.

Where the cheese can be cut, a narrow wedge reaching from the edge to the centre of the cheese will more nearly represent the average composition of the cheese than any other sample. This may be chopped quite fine, with care to avoid evaporation of water, and the several portions for analysis taken from the mixed mass. When the sample is taken with a cheese tryer, a plug taken perpendicular to the surface one-third of the distance from the edge to the centre of the cheese should more nearly represent the average composition than any other. The plug should either reach entirely through or only half way through the cheese. For inspection purposes the rind may be rejected, but for investigations, where the absolute quantity of fat in the cheese is required, the rind should be included in the sample. It is well, when admissible, to take two or three plugs on different sides of the cheese, and, after splitting them lengthwise with a sharp knife, take portions of each for the different determinations.

Determination of Water.

From 5 to 10 grms. of cheese should be taken, and placed in thin slices in a weighed platinum or porcelain dish which contains a small quantity of freshly ignited asbestos, to absorb the fat which may run out of the cheese. This is then heated in a boiling water oven for ten hours and weighed; the loss in weight shall be considered as water. Or, if preferred, the dish may be placed in a desiccator over concentrated sulphuric acid and dried to constant weight. In some cases this may require as much as two months. The acid should be renewed when the cheese has become nearly dry.

Determination of Ash.

The dry residue from the water determination may be taken for the ash. If the cheese be rich the asbestos will be saturated therewith. This may be ignited carefully and the fat allowed to burn off, the asbestos acting as a wick. No extra heat should be applied during this operation, as there is danger of spurting. When the flame has died out the burning may be completed in a muffle at low redness. When desired, the salt may be determined in the ash in the manner specified for butter.

Determination of Fat.

Take 5 to 10 grms. of cheese and grind it in a small mortar with about twice its weight of anhydrous copper sulphate. The grinding should continue until the cheese is finely pulverised and evenly distributed throughout the mass, which will have a uniform light blue colour. This mixture is transferred to a glass tube which has a strong filter paper, supported by a piece of muslin, tied over one end. Put a little of the clean anhydrous copper sulphate into the tube next to the filter before introducing the mixture containing the cheese. On top of the mixture place a tuft of ignited asbestos, and place the tube in a continuous extraction apparatus and extract with anhydrous ether for fifteen hours. Dry the fat obtained at 100° to constant weight.

Determination of Casein.

Make a determination of nitrogen by the Kjeldahl method, taking about 2 grms. of cheese, and multiply the result by 6·25 for casein.

Other Constituents.

The sum of the percentages of the different constituents, determined as above, subtracted from 100, will give the amount of organic acids, milk sugar, &c., in the cheese.

* Official Methods of Analysis adopted by the Association of Official Agricultural Chemists (American) at its Meeting at Chicago, August, 1893.

THE DETERMINATION OF IODINE.

By A. VILLIERS and M. FAYOLLE.

The separation and determination of hydriodic acid in presence of the two other hydracids present very considerable practical difficulties. Various methods have been proposed for their removal.

Duflos displaces the iodine by means of ferric chloride, collects this iodine in a solution of potassium iodide, and titrates the liquid thus obtained by means of sodium thiosulphate. But the results are generally too low on account of the difficulty of the volatilisation of the vapours of iodine.

The method proposed by some authors, depending on the use of nitrous acid for liberating the iodine, presents, also, certain inconveniences. This reagent, which requires special preparation, not being without action on hydrobromic acid, and the presence of nitric acid which often accompanies it, may occasion an oxidation of the iodine.

By combining the method of Duflos, with the use of carbon disulphide as solvent, we have obtained a procedure which enables us to determine in a simple and expeditious manner hydriodic acid in presence of the other hydracids. The results are not inferior in accuracy to those given by the direct determination of free iodine by sodium thiosulphate, one of the most accurrate of those employed in volumetric methods. It seems to us much preferable to the gravimetric methods generally in use. The method founded on the displacement of iodine

by chlorine in silver iodide presents the inconveniences inherent in every indirect method. As for the direct process for separating the iodine as palladium iodide, all chemists who have used it are aware of its disadvantages. The method of operation at which we have arrived is the following:—

The solution to be titrated, which must be free from nitric acid, is placed in a bulb with a glass cock, carefully lubricated, into which some carbon disulphide has been previously introduced. We then add a slight excess of a solution of ferric chloride *containing no free chlorine, e.g.*, 5 c.c. of a semi-normal solution for 1 decigrm. of iodine. The carbon disulphide is then decanted after agitation, and a fresh quantity is added in its stead. The liquid is thus exhausted until a last portion of carbon disulphide is no longer coloured after agitation. Four washings are in general sufficient. The carbon disulphide collected in a second tabulated bulb is washed with a little water to remove the traces of ferric chloride which may have been carried away in the previous exhaustion, and the carbon disulphide thus washed is decanted into a flask with a ground-glass stopper, the drops which have not come together being rinsed out by the addition of a small volume of carbon disulphide. This washing with water is needless if absolute accuracy is not required, as the error which may result from its omission does not exceed one-fiftieth if the decantation has been effected with care. Ordinary tabulated bulbs may be used.

The dissolved iodine is determined directly by means of a solution of sodium thiosulphate, previously standardised. The decolouration of the carbon disulphide is effected very distinctly by agitation.

The accuracy of the determination is not affected by the quantities of hydrochloric and hydrobromic acid present. We have, in fact, obtained the following results with a solution of hydriodic acid prepared by saponifying a known weight of hydriodic ether:—

	Iodine in 1 c.c.
According to weight of hydriodic ether.. ..	0·12152
Determined as silver iodide	0·12136
Determined by ferric chloride and thiosulphate	0·12137
Determined in presence of 10 per cent HBr and 10 per cent HCl	0·12158

If the three halogens have been precipitated as salts of silver we operate upon the hydracids reproduced by means of sulphuretted hydrogen, the excess of which is expelled by ebullition. If we have taken care to dilute sufficiently, the loss of hydracids by volatilisation may be safely neglected.—*Comptes Rendus*, cxviii., 1332.

ON THE ORIGIN OF GOLD NUGGETS.*

By A. LIVERSIDGE, M.A., F.R.S.,
Professor of Chemistry in the University of Sydney.

(Concluded from p. 8).

Conclusion.

WHEN the metallic sulphides and arsenides are used to reduce the gold solution, there is no real necessity for the gold plate or nucleus, since the film of gold which immediately forms on the mineral acts as the negative element of the couple; but it is convenient to use the gold nucleus, inasmuch as the gold is deposited more quickly, and in a form convenient for weighing, as it is free from admixture with other substances; the nucleus merely requires to be washed, dried, and weighed. When substances like powdered granite, glass, clay, sandstone, &c., are used, the gold plate or nucleus is necessary to form the galvanic couple (although a weak one) and to collect the gold.

The gold reduced by means of phosphorus in ether from very dilute solutions has quite a different appearance to that reduced by the sulphides and other substances given in the preceding experiments; the gold is reduced in such a finely divided state that it imparts a blue or purple tint to the water, and may take many years to completely precipitate and yield a clear solution. Some which I precipitated as far back as 1884 still have the gold in suspension.—(A. Liversedge, "On the Removal of Gold from Suspension and Solution by Fungoid Growths," *Report of the Aust. Assoc. Advt. of Science*, 1890, p. 399, *et seq.*).

When the solution of gold is stronger, the gold comes down more quickly, and after a time becomes more or less crystallised, as in the following case:—The gold reduced from a 1 per cent solution of the chloride of gold and sodium by phosphorus in ether, and which had been standing from September, 1889, to April 28th, 1893, or three and a half years, was seen under the microscope to be made up of a mass of narrow ribbons of gold, more or less matted together. The ribbons were of bright, lustrous, metallic gold, and fairly uniform in size; mixed with them were a few rounded particles or beads of gold and some octohedral crystals.

In another and weaker solution (15 grains of the double solution and gold chloride to 15 ounces water), which was allowed to stand for three and a half years, from October, 1889, to April, 1893, the gold was deposited in the form of masses of octohedrons, more or less well formed, and large enough to be seen with an ordinary pocket lens.

In the preceding experiments only the difference in the weight of the nucleus is taken into account, the amount of gold reduced and deposited upon the sulphide or other reducing agent is neglected; in some cases the quantity was very large, but no attempt was made to ascertain the amount as the results were not required in this investigation. The question to be answered by the experiments was merely whether a nucleus of gold immersed in a solution of gold, and in the presence of, or in contact with, a substance (such as might be met with under natural circumstance), would increase in weight: this has been answered in the affirmative, and I think we can safely say that a nucleus of gold in an alluvial deposit, or in a vein in contact with any of the foregoing substances or other similar bodies, would tend to increase in size so long as the supply of gold in solution was maintained, and that masses as large as the largest known nuggers, or indefinitely larger, might be so formed. My own opinion, however, in spite of this, is that the large nuggets have not been so formed, but have been set free from veins, and have acquired their rounded and mammillated surfaces by attrition, the main outline being due to the original form of the mass when liberated from its matrix. Nuggets may have also received deposits of gold from solution, but such deposits have, I think, made no material alteration in the size of the larger nuggets.

The advocates of the hypothesis is that the large nuggets have been formed *in situ*, and they support it by the following amongst other arguments:—

1. That the large nuggets have been found to have a different chemical composition to the vein gold.

Undue weight seems to have been attached to this; the dissimilarity in composition between nuggets and vein gold is usually but small and immaterial, and sometimes the vein gold is even richer than the alluvial. The variations certainly do not show that the nuggets have necessarily had a different origin.

With finely divided alluvial gold there is a greater difference in composition: this may be due to the silver and other impurities having been partly removed by solution; the greater surface exposed by the gold dust and grains would of course facilitate their elimination.

2. That the large nuggets have all been found far removed from the nearest vein.

This is an argument of no great importance, and it is

* A Paper read before the Royal Society of New South Wales, September 6, 1893.

already answered in the preceding pages; the reef from which they have been derived may have been entirely denuded away, or so covered with other material as to be inaccessible.

3. It is urged that if nuggets had been derived from veins their forms would be different, and especially that they would retain traces of crystalline form and roughness within the cavities, and would not possess mammillated surfaces.

As I have pointed out in another paper ("On the Condition of Gold in Quartz Veins," p. 15), it is very unusual to find any trace of crystalline structure in the gold set free from veins. Roughness, of course, we do meet with in vein gold, but when the gold weathers out from the reef this is gradually lost by abrasion; the projecting points of soft malleable gold are flattened down and rounded off rather than ground away in powder, as in the case of hard and brittle substances, and the nuggets would necessarily acquire a mammillated appearance.

It is quite true that heavy nuggets would not be so easily carried by currents as ordinary pebbles and boulders, still they would be moved and rolled occasionally, by masses of rock forced against them, also by being undermined and falling over; further, although perhaps not moving much themselves, they would be subjected to nearly as much abrasion by the constant attrition of other and lighter pebbles grinding over them. The cavities in such nuggets would also be smoothed off and rounded out by the constant stream of water-borne sand and pebbles searching every crevice, acting much like the sand-blast, but less quickly; as the nugget fell over from time to time all parts of its surface would be abraded in turn.

To bring this about I do not think it is necessary to assume, with Sir Roderick Murchison and Prof. Egleston, that the violence of the old currents was greater than that of those of the present day; when in flood, streams of the present day are quite powerful enough to shift, in the manner described, the largest nugget which has yet been found; even in their normal condition, existing streams would eventually bring about the form and general appearance possessed by nuggets.

4. It is stated that large nuggets are much more common than large masses of gold in veins.

As I have already shown, large masses, nearly equal in weight to the largest nuggets, have been met with in veins, and probably will be again; the gold found in alluvial deposits may represent the contents of hundreds of feet (in height) of vein stuff which has been removed by denudation.

The vein stuff removed by the miner is infinitesimal in comparison with the amount which has been removed by geological agencies; and if we could by any means make a fair comparison between the two, we should probably find that the proportion of large masses met with in veins is not unequal to that found in alluvial deposits.

After answering the arguments brought forward to show that nuggets have had a different origin to vein gold, many reasons may be brought forward to show that nuggets have been derived from veins. It has already been pointed out that all the large nuggets have had more or less quartz attached to them, which shows that they have either been set free from quartz veins or else that the two substances had been deposited together in the alluvial, and, as we have no proof of quartz—*i. e.*, of the particular kind associated with gold nuggets—being deposited otherwise than in reefs, the latter explanation is hardly tenable.

Many of the water-worn quartz boulders, pebbles, and sand found with gold, are admitted to have come from gold-bearing rocks and reefs; that being so, why should we seek for another origin for the associated water-worn pebbles of gold?

Further, if it be contended that all the large nuggets have been formed *in situ*, from gold in solution, then we may ask, What has become of the large masses of gold which must have been set free from the veins by denudation?—masses which we know must have been comparable to the largest nuggets, for several such have been mined, and, as Prof. Whitney has pointed out, Why is alluvial gold not found as plates and strings if it has been deposited *in situ*?

There is no doubt in my mind, first, that gold is present in meteoric waters, although, as already stated, no absolute chemical proof of its presence has been brought forward (except in the case of sea-water), for it is found in recently formed pyrites and other deposits, and could only have got there from solution. In sea-water it is thought to be held in solution by iodine; but its condition in land-waters is uncertain—it may be as chloride, sulphide, silicate, or other compound.

The recently formed pyrites containing but a trace of gold might, in theory, eventually be wholly replaced by a mass of gold possessing a mammillated structure and the appearance of a nugget; but practically I do not think this has occurred.

Artificial nuggets of quite large size, I am sure, could be made in a few years by almost any of the methods followed for obtaining thin films of gold on sulphides, plates, and particles of gold, as detailed in this paper, and I think that in places gold is being so deposited at the present day, but I feel sure that the large nuggets have not thus been formed *in situ*; they have been set free from reefs, and any small addition of gold that they may have derived from meteoric water has been quite immaterial, and may be neglected. In the case of gold grains and dust it may be different, for such expose a much greater surface, and the "electroplating" may have had an appreciable effect in increasing the amount of such gold.

THE DETECTION AND SEPARATION OF ARSENIC ASSOCIATED WITH ANTIMONY AND TIN.*

By F. A. GOOCH and B. HODGE.

Upon the well-known fact that hot strong hydrochloric acid is capable of dissolving the sulphides of antimony and tin while exerting solvent action to a very slight degree upon arsenious sulphide is based the simplest and most rapid method in common use for the separation of arsenic from antimony and tin. Unfortunately, however, the forcible treatment necessary to bring about the solution of large amounts of antimony is sufficient (Rose-Finkener, *Anal. Chem.*, ii., 423) to dissolve small quantities of arsenious sulphide, so that for the purposes of general analysis the method is inadequate.

Koehler (*Zeit. fur Anal. Chemie*, xxix., 192) has shown that only the arsenic is precipitated, and that very completely, when hydrogen sulphide acts upon the solution of arsenious and antimonious salts in hydrochloric acid of 20 per cent strength; but the adaptability of Koehler's treatment to the detection of arsenic in the ordinary course of analysis is limited by the necessity of so constituting the solution to be tested that hydrogen sulphide shall occasion no deposit of free sulphur to conceal or be mistaken for a precipitation of arsenious sulphide.

In the course of analysis the mixed sulphides of arsenic, antimony, and tin remaining after the removal of the sulphides insoluble in alkaline sulphides and recovered from solution by the action of hydrochloric acid, require for their complete solution the action of an oxidising agent which must, of course, interfere with the immediate use of Koehler's method.

If simple means can be found for the destruction of the excess of the oxidising agent and the simultaneous re-

* Contributions fom the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, xlvii., May, 1894.

duction of the arsenic and antimony to the lower condition of oxidation, it is plain that the test for arsenic by passing hydrogen sulphide into the solution of antimony and tin in hot hydrochloric acid of half-strength should be sure and easy.

In a former paper from this laboratory (Gooch and Danner, *American Journal of Science*, xlii., 308) a method was described for the quantitative separation of arsenic from antimony, based upon the reduction and volatilisation of salts of arsenic by the action of a current of gaseous hydrochloric acid upon the solution containing potassium iodide. It is this reaction—the reduction of arsenic and antimony and the volatilisation of the former by the simultaneous action of potassium iodide and hydrochloric acid—which we have now endeavoured to apply in simple form to the rapid detection of small amounts of arsenic associated with antimony and tin. We have studied the effect of repeated distillations of small portions of concentrated hydrochloric acid upon mixtures of the salts with potassium iodide.

The apparatus which we employ is essentially the distillation apparatus of Mohr, and consists of a 25 c.m.³ flask fitted by means of a rubber stopper to a pipette bent, drawn out at the lower end, and dipped into a test-tube which is at the same time supported and cooled in a flask partly filled with water. The pipette tube is wide enough (about 0·7 c.m. in diameter) to prevent the formation of bubbles within it, and the bulb, holding about 20 c.m.³, is sufficiently large to retain any liquid which may be momentarily forced back by the accidental cooling of the flask during the distillation.

In the test experiments recorded below the arsenic was introduced into the flask in the form of arsenic acid dissolved with 3 grms. of potassium iodide in 5 c.m.³ of water, an equal volume of the strongest hydrochloric acid (sp. gr. 1·20) was added, the distillation was carried nearly to dryness, and the distillate was condensed in 10 c.m.³ of a mixture of strong hydrochloric acid and water in equal parts. The iodine evolved during the distillation was bleached by the addition to the distillate of stannous chloride dissolved in hydrochloric acid of half-strength, and hydrogen sulphide was passed to precipitate the arsenic if present. The residue in the flask was treated with 10 c.m.³ of the strongest hydrochloric acid and the process of distillation was repeated, but this time the distillate was condensed in 10 c.m.³ of water in order that the final acidity of the liquid should be that of acid of half-strength, and so after bleaching by stannous chloride immediately available for the test for arsenic by hydrogen sulphide. Subsequent treatments of the residue were carried out similarly until arsenic ceased to appear in the distillate.

The results of Experiments 1 to 5 show that four successive distillations of 10 c.m.³ portions of the strongest acid are enough to transfer 0·01 grm. of arsenic completely to the distillate, while a single distillation appears to be sufficient to volatilise anything less than 0·003 grm.

Experiments 6 to 9 made similarly with antimony, taken in the form of purified tartar emetic and oxidised by iodine in alkaline solution previous to treatment, either alone or with arsenic, show that antimony is discoverable in the residues when even so little as 0·0001 grm. of that element is originally introduced, though it was very evident that a portion of the antimony may pass to the distillate when much of it is present in the flask. Indeed, when large quantities of antimony are treated the appearance of the brownish red fumes of antimonious iodide in the distilling tube may serve as a very good indication that the concentration should go no farther, since the antimonious iodide may, if it reaches the receiver in quantity, impart to the distillate a colour which is not discharged, by the stannous chloride used to bleach the iodine and which makes it necessary to look subsequently for a precipitate of arsenious sulphide in a liquid of its own tint. The amount of antimony volatilised seems to be proportioned to the amount present, and, if the distillation is properly conducted, enough antimony remains in the residue to be found if it was originally present in discoverable quantity.

The results of similar work with tin alone, and with tin and arsenic, are recorded in Experiments 10 to 15, and the evidence goes to show that, though like antimony it may pass to the distillate under the conditions, enough tin always remains to be found in the residue if the amount originally taken was discoverable.

	Arsenic taken as H_3O_3AsO. Grm.	Antimony taken as H_3O_3SbO. Grm.	Tin taken as $SnCl_4$. Grm.	Precipitation by H_2S in successive distillates.	Precipitation by H_2S in the residue dissolved in water.
1.	0·0001	—	—	I. Found. II. None.	None.
2.	0·0033	—	—	I. Found. II. None.	None.
3.	0·0050	—	—	I.—III. Found. IV. None.	None.
4.	0·0100	—	—	I.—IV. Found. V. None.	None.
5.	0·1000	—	—	I.—VII. Found. VIII. None.	None.
6.	—	0·0001	—	I. None.	Distinct colour.
7.	0·0050	0·0001	—	I.—IV. Found. V. None.	Distinct colour.
8.	0·0001	0·4	—	I. Found. II. None.	Large.
9.	0·0100	0·4	—	I.—IV. Found. V. None.	Large.
10.	—	—	0·0001	I. None.	Distinct colour.
11.	0·0100	—	0·0001	I.—IV. Found. V. None.	Distinct colour.
12.	0·0001	—	0·0005	I. Found. II. None.	Distinct.
13.	0·0100	—	0·0005	I.—IV. Found. V. None.	Distinct.
14.	0·0001	—	0·5	I. Found. II. None.	Large.
15.	0·0100	—	0·5	I.—IV. Found. V. None.	Large.

It is plain that a single distillation, which may easily be completed in five minutes, is sufficient to discover the presence of 0·0001 grm. of arsenic associated with so much as 0·4 grm. or 0·5 grm. of antimony or tin.

It is also evident that amounts of arsenic not exceeding 0·003 grm. may be completely removed from the residue by a single distillation. When larger amounts of arsenic are to be removed, so that the tin and antimony may be obtained free from that element, the result may be accomplished by repeating the distillation sufficiently; or, inasmuch as only a little iodine remains after the first distillation, the end may be attained by dissolving the residue in hydrochloric acid of half-strength, bleaching the iodine with exactly the necessary amount of sulphurous acid or sodium thiosulphate (since the use of the stannous chloride is here precluded), and passing hydrogen sulphide.

Derivatives of the Series of the Oxazines and Eurhodines.—Ch. Lauth.—The author has obtained a blue-violet colouring matter, very soluble in water and alcohol, sparingly soluble in sodium carbonate, with a reddish violet. Ammonia dissolves it better. It is soluble with a very red-violet in strong sulphuric acid, with an olive-green in hydrochloric acid. Dilute acids dissolve it with a pure blue. It dyes silks, wool, and cotton if prepared with tannin.—*Bull. de la Soc. Chim.*, xi.-xii., No. 7.

NOTICES OF BOOKS.

A Dictionary of Medicine; including General Pathology, General Therapeutics, Hygiene, and the Diseases of Women and Children. By Various Writers. Edited by Richard Quain, Bart., M.D. Lond., LL.D. Edin., F.R.S., President of the General Council of Medical Education. Assisted by Frederick Thomas Roberts, M.D. Lond., B.Sc., F.R.C.P., and J. Mitchell Bruce, M.A. Aber., M.D. Lond. New Edition, Revised throughout and Enlarged. Two Vols. 8vo, pp. 2483. London: Longmans, Green, and Co., 1894.

This elaborate work is to a great extent concerned with subjects which lie outside of our purview. But judging from the important sections treating on questions to which we have given special attention, we feel free to pronounce the whole of remarkably high value.

Under the head "Adipocere" we note the curious fact that the Illinois limestone is "composed of coral; in each cell a particle of oil is sealed up."

Absinthism is duly noticed; but notices, however truthful and emphatic, will effect little until the importation and sale of absinth is prohibited. Why is the "Temperance" interest mute on the subject?

To mistake the root of aconite, or monks'-hood, for horse-radish is an instance of intolerable stupidity.

The Orange Free State is recommended as a sanitary resort for invalids. We have known it, however, fearfully decimated by an epidemic of diphtheria. The dust-storms of South Africa and Australia are duly noticed as a serious peril. Dust conveys infection in the open country just as it propagates fires and explosions in coal-mines and flour-mills.

Under Albuminuria a saturated solution of picric acid is recommended as a decisive test for albumen in the urine in doubtful cases.

Under Alcohol we are reminded that the experiments of Lallemand, Perrin, and Duroy have been proved to be erroneous by Anstie and Dupré, and more recently by Bodlaender.

Under the head of Alimentation we are reminded that Liebig's classification of foods into plastic and respiratory has lost much of the scientific value which it was at one time supposed to possess.

The varying action of the Alkaloids is summarised in the proposition that where the spinal system predominates most of the opium alkaloids act as convulsants, whilst in the higher mammals they affect the brain and have a soporific action.

The accusation of poisonous properties brought against the aniline colours is decidedly too sweeping, and as regards colours free from arsenic must be pronounced exaggerated, as may be learnt from the published researches of Dr. Grandhomme.

The article on Climate is exceedingly valuable; but we can scarcely accept the statement that the inhabitants of warm countries are "indolent and apathetic." China is a warm country, but its inhabitants carry industry to an excess.

The effects of coal-gas penetrating through the soil may, it is shown, occasion disease and even death in houses into which no gas-pipe has been conveyed. Water-gas, recently introduced, is rightly characterised as extremely dangerous.

The important question of contagion is ably handled. The writer does not forget to remind us that whilst the law provides due penalties for such as turn polluted matter into open streams or lakes, it omits all the offences of polluting wells or springs by underground impurities.

No sufficient care is taken in times of any epidemic to restrain the distribution of tradesmen's circulars, tracts, books from libraries, &c. Many people during convalescence, to while away tedious hours, obtain books from a library, and return them possibly saturated with pathogenic microbia.

Public elementary schools are also efficient foci of infection. The pupils of private schools, if they have been suffering from scarlatina, diphtheria, or other zymotic disease, are not urged to return to school until they are no longer capable of diffusing disease. But the parents of School-board pupils are sometimes worried and threatened by officials into sending their children back to school long before it is completely safe. Perhaps this evil might be lessened if the Medical Officer of Health were *ex officio* entitled to a seat on the Board.

The toxic properties of copper do not seem to be placed beyond doubt. Copper poisoning, it is admitted, is less common than are the evil effects of lead.

Chromium and its compounds seem to have been overlooked as possible sources of injury to health. This is the more to be regretted since these compounds are now largely used in the arts, and may find their way into water-courses.

Cantharides are duly described as a serious poison; but the fact that in countries where they are plentiful they may be devoured by ducks, turkeys, &c., so as to render the flesh of these birds dangerous to man has been overlooked.

Under the head of Diet the authors do not prophesy smooth things to the various schools of dietetic reformers, especially the so-called vegetarians.

The article on Entozoa is of interest not merely scientifically, but from a practical point of view. These intruders are introduced into the human body by eating underdone beef and pork and certain kinds of fish. The dreadful trichinæ are rare in Britain, but fairly common in Germany, where it is customary to eat raw ham, sausages, and what is called "hackfleisch," *i.e.*, minced raw pork. The guinea-worm may be avoided by drinking no water which has not been boiled and filtered.

The article on Epidemics opens up some interesting questions, above all the concurrence or mutual antagonism of different diseases. Thus measles concurs very frequently with other diseases, diarrhœa with all other epidemics except small-pox, &c.

We are glad to find that the authors recognise mosquitos and blood-sucking flies in general as active in introducing *Filaria sanguinis Hominis* into the human circulatory system.

As regards hay-fever the question may be asked, whether susceptibility to this harassing disease may not be connected with overwork?

Under the head "Puberty" Dr. T. Moore Maddon writes:—"At that period of life the present cramming system of education frequently predisposes to insanity, the organ of the mind being goaded into premature activity and overstrained in the effort to pass some competitive or other examination deemed essential to entrance on official, commercial, or professional life."

In an elaborate essay on Public Health we find utterances which are gravely to be regretted. In a hot, dry climate like that of many parts of South-Western Asia, Northern Africa, and most parts of Australia, irrigation is excellent for the treatment of sewage. But in a cold, damp climate like that of Britain precipitation is decidedly preferable. It can produce effluents sufficiently pure for admission into any stream, and so far from the valuable manurial ingredients of the sewage being "utterly wasted," we have met with sewage manures obtained by precipitation which contain 3 per cent of ammonia, and phosphoric acid equal to 5 per cent of tricalcic phosphate. This result is obtained on the large scale and without the addition of either nitrogenous or phosphatic matter.

There is in these two goodly volumes little indeed to which we can take exception, but, on the other hand, much which we must pronounce of the highest value.

The Laboratory Guide: a Manual of Practical Chemistry for Colleges and Schools. Specially Arranged for Agricultural Students. By Arthur Henry Church, M.A., F.R.S., Professor of Chemistry in the Royal Academy of Arts in London, some time Professor of Chemistry in the Royal Agricultural College, Cirencester, &c., &c. Seventh Edition, Revised. London: Gurney and Jackson (Successors to Van Voorst), 1894. Small 8vo, pp. 292.

The "Laboratory Guide" is no doubt most favourably known to a large majority of our readers—certainly to all who have studied the theory or the practice of agricultural chemistry. They will find the present edition decidedly improved. Thus in Part I. an additional lesson on soils has been introduced, and the Kjeldahl and the Ruffle methods of determining nitrogen are given. The account of the old citric acid method for the determination of phosphorus pentoxide is omitted. The same fate has befallen the method for extracting the fat from desiccated milk, which in view of the procedures of Adams and Werner-Schmid may be considered as superseded.

The instructions for the analysis of water are enriched by a brief reference to the biological method, and of the appearance of the sediment under the microscope. Under many circumstances the biological examination can scarcely be overlooked if sufficient time is allowed to the analyst.

We do not know of any work in the English language which is equal—not to say superior—to that of Prof. Church as a guide to the agricultural student.

Thermodynamics of Reversible Cycles in Gases and Saturated Vapours. Full Synopsis of a Ten-weeks Undergraduate Course of Lectures Delivered by M. I. Pupin, Ph.D. Arranged and Edited by Max Osterberg, Student in Electrical Engineering, Columbia College. New York: John Wiley and Sons, 1894. London: Gay and Bird. Small 8vo, pp. 114.

This little work is designed for the use of persons conversant with the higher mathematics, and for such it will doubtless prove satisfactory. For all others it is simply unintelligible.

We must, however, with regret call attention to a passage which occurs in the introduction and again at the very close of the work. The author speaks in both these places of the "science of caloric engineering." The accepted authorities on method have pointed out clearly and satisfactorily the distinction between Science and Art, the former seeking to reveal and interpret what exists, and the latter attempting to apply or to modify it to man's purposes. Hence engineering cannot rightly be called a science. The term "caloric"—a survival of the phlogiston of former days—is now tolerated merely in the state of "calorie," a name selected for a standard quantity of heat. Used in any other sense it is a return to a theory which the author rejects in his first chapter.

Alembic Club Reprints, No. 6.—The Decomposition of the Fixed Alkalies and Alkaline Earths. By Humphrey Davy (1807—1808). Edinburgh: W. F. Clay, 18, Teviot Place. London: Simpkin, Marshall, and Co., Lim., 1894.

We find in these days no little difficulty in realising the facts that a century has not yet gone by since potash and soda, the fixed alkalis, as they were commonly called, were still accepted as simple or elementary substances, and that careful and prolonged research was needed to prove that they were metallic oxides. This discovery was of an epoch-making character. It established the analytical value of electric currents, and paved the way to the decomposition of the alkaline earths.

In his experiments for ascertaining the properties of the new metals, Davy shows himself from his best side. Some persons have attempted to argue that anyone having the great batteries of the Royal Institution at his command could have done the same thing. This is an idle cavil. Davy had in the outset at command merely the rudimentary chemistry of the first years of the present century. Few men indeed can soar above the limits of the intellectual atmosphere which surrounds them. In Davy's time it was still necessary in considering any novel fact to keep the phlogistian hypothesis in view, and to demonstrate its inability to explain the new discoveries. As a proof how much even our simplest observations are dominated by preconceived views, we may mention a fact not recorded in the little book before us:—A *savant* of those days, having been shown a specimen of potassium, remarked its metallic lustre, and added "and how ponderous!"

Davy's experiments on the decomposition of the alkaline earths were successful, though he never obtained the corresponding metals on a satisfactory scale. He devised the names barium, strontium, and calcium, which have remained in use. He does not accept magnesium for the base of magnesia, as it had been very unhappily applied by Bergmann to metallic manganese. It is to be regretted that no one has yet ventured to end the confusion between magnesia and manganese by striking off the last syllable of the latter. We have already spoken of manganic acid; why not be consistent and have manganum for the metal? Ammonia seemed to Davy a triple compound of hydrogen, nitrogen, and oxygen.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxviii., No. 26, June 25, 1894.

The Session of Monday, June 25, was, on the motion of M. Loewy, the President, broken off on account of the assassination of M. Carnot.

Bulletin de la Société Chimique de Paris. Series 3, Vols. xi.-xii., No. 11.

Certain Tartaric Ethers with Aromatic Radicles.—M. Freundler.—The author, in studying the variation of rotatory power in the series of tartaric ethers, has prepared a number of derivatives in which the substituted acid radicles belong to the aromatic series. He has particularly studied the methylic, ethylic, and propylic ethers of the dibenzoyltartaric, diphenylacetyl tartaric, and diphenyl paratoluyltartaric acid, as also the corresponding anhydrides. The anhydrides are prepared by heating dry pulverised tartaric acid with three times its weight of chloride of the acid. They can be purified only when solid, as they decompose on distillation. The author has examined several of these ethers cryoscopically in ethylene bromide, benzene, acetic acid, and nitrobenzene, and he has again observed a relation between the cryoscopic and polarimetric anomalies.

Rotatory Power of Dissolved Substances.—M. Freundler.—When the solvent does not affect the rotatory power of the active body, the figure of $(\alpha)_D$ is distinctly independent of the concentration, as are also the cryoscopic numbers. But if the solvent alters the rotatory power, $(\alpha)_D$ will vary with the concentration. In the case of the tartaric ethers, the more the concentration increases the more the figure given by the solution approximates to the normal power given by the ether itself. Hence there results a very simple means of ascertaining if we meet a real power of the dissolved substance or if the act of solution has modified this power in any manner. It is merely

necessary to make two determinations of $(\alpha)_D$ at two different concentrations.

Aminofumaric Derivatives.—R. Thomas-Mamert.—This lengthy paper requires the accompanying diagrams.

Certain Metallic Campholates.—M. Guerbet.—The author studies the ammonium, potassium, sodium, barium, strontium, calcium, magnesium, zinc, copper, nickel, and cobalt campholates.

Ethers of Campholic Acid.—M. Guerbet.—The author examines the speed of etherification, its limit, the saponification of the campholic ethers, the behaviour of ethyl campholate with aqueous and alcoholic potassa, with hydrochloric acid, with gaseous hydriodic acid, the preparation of the campholic ethers, and gives a particular account of the methyl, ethyl, isopropyl, isobutyl, amyl, and phenyl campholates.

The Blue Lakes Derived from Dibromogallanilide, and Certain Blue Reactions of the Polyphenols in Presence of Alkalis.—P. Cazeneuve.—If to an alcoholic solution of dibromogallanilide we add cautiously ammonia or a solution of potassa or soda, there appears an indigo blue colouration, easily altered by an excess of air or of base; this solution in time turns green and then yellow. Lime water and baryta water give under the same conditions a white precipitate, which quickly turns to a fine blue on agitation with air. A weak acid or a current of CO_2 decomposes the lake and liberates an acid of a gooseberry-red. The zinc lake is much more stable.

Aromatic Sulphones.—P. Genvresse.—In this investigation the author has obtained for the first time and examined the sulphones of diphenylmethane, of benzylidene bromide, of triphenylmethane, of triphenylcarbinol, of hexanitric triphenylmethane, of hexanitric trephenylcarbinol, of pararosaniline and its leuco-base, and lastly, simultaneously with H. H. Paehl and Eberhard, though in another manner, he has obtained the sulphones of ethyl benzene and isopropyl benzene.

A New Reaction of Colchicine.—Ernest Barillot.—The suspected substance, separated in the state of base, is ground up with 0·25 grm. oxalic acid and 1 c.c. SO_4H_2. The mixture placed in a small closed tube is kept for an hour in the oil-bath at 120°. The tube is taken out, the colour of the mixture is examined, water is added, and then alcoholic soda in excess. If colchicine is present, the colour in the cold is a gold-yellow; after heating, a deep brown bordering on red, and is not modified by the addition of water. If the aqueous solution is treated with an alkali, then re-acidified with acetic acid, it yields a yellow colouring matter soluble in chloroform. The chloroform leaves it in the state of a yellow powder, which turns to a raspberry-red if moistened with nitric acid of specific gravity 1·4.

New Method of Determining Salicylic Acid and the Salicylates.—L. Barthe.—This memoir will be inserted *in extenso*.

MISCELLANEOUS.

Welcome Beneficence.—Mr. Ludwig Mond, F.R.S., V.P.C.S., has distinguished himself by endowing scientific research on a scale of princely magnitude. He purchased last year the freehold mansion of the Earl of Albemarle, in Albemarle Street, bordering on the premises of the Royal Institution, and is about conveying it in fee simple to the Royal Institution. He will also defray the whole expense of converting it into a laboratory for chemical and physical research, to be called the "Davy-Faraday Research Laboratory," and of fitting it up with all appliances for the conduct of research upon a large scale. He will further endow the new laboratory with an income sufficient to meet all demands of rates, taxes, and maintenance; and, secondly, with funds to pay the salaries and incidental expenses of a competent scientific staff, and to carry on the operations of the proposed Institution. The laboratory will be open to all persons who, in the judgment of the Council of the Royal Institution, are competent to undertake chemical and physical research, persons who have already done original scientific work receiving the preference. The value of the premises and funds thus handed over to the Royal Institution in trust for the nation exceeds £100,000.

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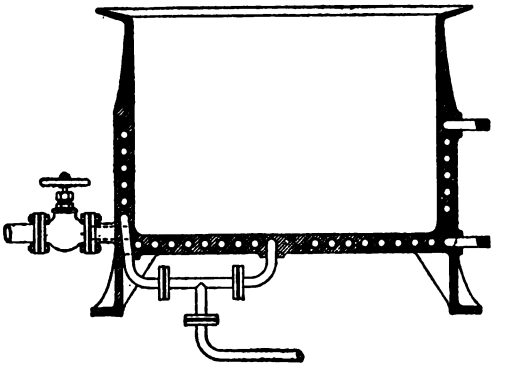

Mr. C. R. ALDER WRIGHT, Lecturer on Chemistry and Examiner in Soap to the City and Guilds of London Institute, in his latest edition of "Animal and Vegetable Oils, Fats, Butters, and Waxes, &c." (Charles Griffin and Co., Lim., London, 1894), says:—

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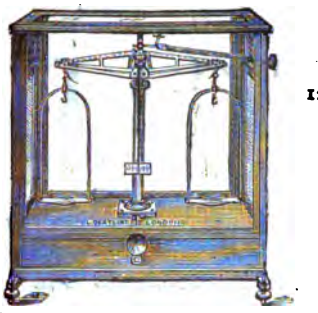

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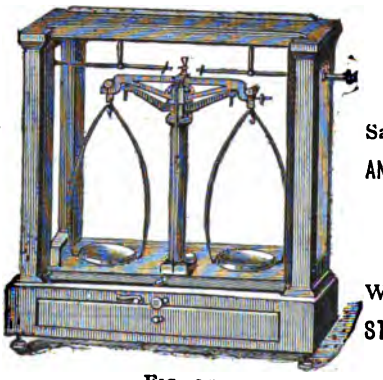

FIG. 3*a*.

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THE CHEMICAL NEWS.

VOL. LXX., No. 1808.

THE COMPOSITION OF ATMOSPHERES WHICH EXTINGUISH FLAME.*

By FRANK CLOWES, D.Sc. Lond.,
Professor of Chemistry, University College, Nottingham.

1. *Introductory Remarks.*

A STUDY of the experiments which have been made to determine the composition of atmospheres, which act extinctively upon flame, shows that in many cases the atmosphere under examination was in contact with water. The solvent action of water on the carbon dioxide present seems in such cases likely to disturb the composition of the mixture. In other cases only the proportion of oxygen in the extinctive atmosphere was noted, and the nature of the diluent gas or gases was not taken into consideration. Experiments were also limited to the flames of a few combustible substances, or where a wider range of different flames were tried, the results reported were only of an approximate and relative nature.

The experimental work, the results of which are summarised in this communication, was undertaken in order to supplement the deficiencies referred to above, with the view of drawing further generalisations, and of furnishing support to those already drawn from previous experiments.

2. *Method of Experimenting.*

The mixtures of air with the extinctive gas were made in a glass cylinder, which was closed by a ground glass plate.

A measured quantity of water, equal in volume to the percentage of extinctive gas to be mixed with the air, was first poured into the glass cylinder. The cylinder was then closed by the plate and inverted in a vessel of water. A light xylonite ball of known volume was then passed up, and the extinctive gas was introduced in sufficient quantity to fill the cylinder. The cylinder was then closed and its contents were mixed by the movement of the ball.

In order to test the accuracy with which any desired mixture of gases could be prepared by this method, two mixtures of air with carbon dioxide were submitted to analysis. They furnished respectively 9·8 instead of 10 per cent, and 69·7 instead of 70 per cent of carbon dioxide.

The experimental flames used were 0·75 in. in height and were gradually lowered into the cylinder, the top of which was finally covered by the plate. The gases were burnt from a platinum jet 1 m.m. in diameter.

* A Paper read before the Royal Society.

The gaseous mixture was considered to be in extinctive proportions if the flame was extinguished during its downward passage, or immediately upon attaining its lowest position in the cylinder. The mixture was considered to contain the *minimum necessary quantity* of extinctive gas, when another mixture containing 1 per cent less of the extinctive gas allowed the flame to continue burning in it for a few seconds only.

The limiting differences between the results of repeated trials corresponded to 1 per cent of the extinctive gas in the air.

This minimum necessary percentage of extinctive gas is recorded below in tabulated form.

It was considered necessary to take the immediate extinction of the flame as the criterion of extinctive power, since the composition of the atmosphere was rapidly affected by the combustion of the flame.

3. *Influence of the Size of the Flame.*

As a matter of convenience, the flames were, in all cases, set to a height of 0·75 inch. But a series of experiments was undertaken with the same flame of varying size, in order to ascertain if the proportion of extinctive gas necessary to extinguish the flame varied with the size of the flame.

The results of these experiments with flames of hydrogen and alcohol, varying from 0·4 in. to 1·5 in. in height, show that the varying dimensions of the flame, within the wide limits included in the trials, are without influence on the proportion of carbon dioxide in the air necessary to produce extinction.

4. *Method of Preparation of Gases Used.*

The carbon dioxide employed for the experiments was prepared in the usual way by the action of diluted hydrochloric acid upon marble. It was washed with water, and was proved to be practically free from air.

The nitrogen was prepared by heating an aqueous solution containing potassium nitrite, ammonium chloride, and potassium dichromate. An analysis of the resulting gas proved that it contained 99·7 per cent of nitrogen.

5. *Results obtained by the Experiments.*

In the accompanying Table the number entered is the average of numerous closely concordant experimental results. The percentage volume of nitrogen in air is taken as 21.

Characteristic differences were observed between the behaviour of wick-fed flames and that of gas-fed flames when they were introduced into an atmosphere which extinguished them. The wick-fed flames gradually diminished in size until they vanished. The gas-fed flames, on the other hand, gradually increased in size, becoming pale and apparently lower in temperature, and then suddenly expired. The extinction of the flame is apparently due in both cases to the lowering of its temperature. This primary cause, however, seems to operate directly in the case of the gas-fed flame, whilst in the case of the wick-fed flame it operates by gradually reducing the amount of combustible gas and vapour produced, and leads ultimately

Combustible substance burnt.	Extinctive proportion of carbon dioxide added to air.			Extinctive proportion of nitrogen added to air.		
	Percentage added.	Percentage composition of mixture:		Percentage added.	Percentage composition of mixture.	
		O	: (N+CO_2).		O	: N.
Alcohol, absolute	14	18·1	81·9	21	16·6	83·4
Alcohol, methylated	13	18·3	81·7	18	17·2	82·8
Paraffin, ordinary lamp oil	15	17·9	82·1	23	16·2	83·8
Colza oil with equal volume of petroleum	16	17·6	82·4	22	16·4	83·6
Candle	14	18·1	81·9	22	16·4	83·6
Hydrogen	58	8·8	91·2	70	6·3	93·7
Carbon monoxide	24	16·0	84·0	28	15·1	84·9
Methane	10	18·9	81·1	17	17·4	82·6
Ethylene	26	15·5	84·8	37	13·2	86·8
Coal-gas	33	14·1	85·9	46	11·3	88·7

to the flame dying from lack of combustible material. The large expansion of the gas-fed flame is evidently due to an attempt to obtain the necessary supply of oxygen in the diluted atmosphere by increasing its own surface.

6. *Theoretical Considerations.*

The following deductions seem to be warranted by the results arrived at in these experiments:—

1. That the extinction of a flame is not determined only by the *proportion* which the inert gas bears to the oxygen of the atmosphere into which it is introduced, but that the *nature* of the inert gas present also influences the result.
2. That carbon dioxide uniformly exerts a more powerful extinctive effect upon flame than nitrogen does.
3. That there is a remarkable uniformity in the proportions of inert gas which must be mingled with air in order to just extinguish wick-fed flames.
4. That this uniformity does not apply to the flames of combustible gases burnt from a jet.
5. That the flames of gases burnt from a jet show no simple relation, as regards the proportion of oxygen present in the extinctive atmosphere, to the relative proportions of oxygen required for their complete combustion.

With regard to the superior extinctive power of carbon dioxide over that of nitrogen, it has been stated that the greater the density of an inert gas which is introduced into air, the less will be the quantity which suffices to arrest combustion. Waldie suggests that this is due to the cooling effect produced upon the flame by the rapidity of diffusion of its heated products increasing as the surrounding atmosphere increases in density. But it is probable that carbon dioxide also surpasses nitrogen in its extinctive effect upon flame in virtue of its higher specific heat, and because of its slower movement owing to its high molecular weight and density. When the heavy gas is mingled with the air, it adds to the density of the mixture, and renders the atmosphere more sluggish in its movement towards the flame to supply the necessary oxygen.

It had been anticipated that in the presence of the hydrogen flame, and possibly of other flames, carbon dioxide would have suffered partial deoxidation, as it is well known to do in the presence of burning magnesium vapour. No such action appeared to occur, else the above relation between the extinctive powers of carbon dioxide and nitrogen could not well exist.

The cause of the comparative uniformity of the proportion of extinctive gas required for wick-fed flames has been already hinted at. The flames are starved of combustible nutriment by the lowering of the temperature of the flame. This cause seems to operate with strikingly similar results upon the different solid and liquid combustibles.

The cause of the want of conformity to theoretical considerations in the case of the gaseous flames fed from jets is not at once apparent.

It is of practical interest to note that the introduction of a minimum of 15 per cent of carbon dioxide into air is necessary to cause it to extinguish ordinary wick-fed flames, the oxygen being reduced by this admixture from the normal proportion of 21 per cent to 18 per cent. For the extinction of a coal-gas flame, however, the addition of 33 per cent of carbon dioxide is necessary, and the oxygen being thus reduced to 14 per cent. The hydrogen flame has far greater vitality, requiring the admixture of 58 per cent of carbon dioxide with air, and the consequent reduction of the oxygen to 8·8 per cent, before it suffers extinction. This fact is of great importance, since it shows that the hydrogen flame in the composite miner's safety lamp (*Roy. Soc. Proc.*, lii., p. 486) may be used as an auxiliary to prevent the loss of flame when the lamp is being carried through mine air containing large proportions of carbon dioxide.

I have to thank one of my senior students, Martin E. Feilmann, B.Sc., for conducting much of the experimental work involved in this research.

(*April* 28, 1894.—Recent experiments seem to prove that a rabbit can breathe with impunity for at least an hour air containing 25 per cent of admixed carbon dioxide (J. R. Wilson, *American Journal of Pharmacy*, l., No. 12). If this is the case, the extinction of an ordinary flame does not prove the surrounding atmosphere to be irrespirable. The introduction of 15 per cent of this gas extinguishes a flame, whilst the air seems to be still respirable, even after it has been mingled with an additional 10 per cent of carbon dioxide.—F. C.)

THE POST-MORTEM DETECTION AND ESTIMATION OF STRYCHNINE.

By ALLERTON S. CUSHMAN.

In the post-mortem detection and estimation of strychnine the greatest difficulty which presents itself is the separation of the alkaloid from the various extractive fatty, sugary, and pigmentary matters derived from the stomach contents or organs under examination. The fact that such small doses as 32 m.grms. (½ grain) and 48 m.grms. (¾ grain) of the sulphate of strychnia have in two well-authenticated cases proved fatal (Blyth, "Poisons, Effects and Detection"), and also that absorption and distribution of the poison through the system begins as soon as it is administered, makes the problem set before the chemist one of unusual difficulty. In case death has occurred with all the well-defined symptoms of strychnine poisoning in the course of an hour or two after the first signs of sickness appeared, the contents of the stomach and bladder generally account for a sufficient quantity of the alkaloid to substantiate the diagnosis. Sometimes, however, strychnine has to be sought in exhumed remains where the evidence as to symptoms or duration of sickness is incomplete or vague. In such a case it has been doubted by some toxicologists that strychnine could be detected at all after long burial and the consequent advanced decomposition of the body. In contradiction of this opinion is the experience of A. H. Allen ("Commercial Organic Analysis," Part II., iii., p. 376), who found the alkaloid in the dust of decomposed human viscera which had lain in a charcoal stoppered vessel for six years. Again lately W. A. Noyes (*Journ. Am. Chem. Soc.*, xvi., No. 2) detected strychnine in an exhumed body after it had been buried for 308 days.

The danger of error has also been noted from the formation of cadaveric alkaloids or ptomaines in decomposed bodies which may in some of their reactions simulate the reactions of strychnine. While this is probably true it is impossible that any chemist would submit an opinion on a case of strychnine poisoning unless all possible tests, chemical, physiological, and morphological, had first been tried, and it is hardly likely that any alkaloid substance other than strychnine itself could be mistaken for it.

In all of the literature on strychnine and its post-mortem separation but little attention is paid to the estimation of quantity, most authorities appearing to consider the detection of the alkaloid sufficient. Undoubtedly where death has occurred accompanied by well-defined ante-mortem symptoms the finding of even much less than the usual fatal dose would seem to be conclusive, since the poison which actually caused death has undoubtedly been distributed and absorbed in doing its work. Quantitative evidence is, however, always valuable and sometimes indispensable before an opinion can be formed or submitted in evidence before a jury.

In the usual method of analysis the material to be examined is extracted with alcohol and some acid. The

aqueous residue that remains after filtering and evaporating off the alcohol is diluted and filtered, necessitating an examination of both filtrate and residue for the alkaloid, the residue sometimes carrying more than the filtrate (*Journ. Am. Chem. Soc.*, xvi., No. 2). The filtrate is then evaporated, the extraction with alcohol repeated, and the filtrate finally made alkaline and extracted with chloroform. The chloroform never separates well from the alkaline liquid at this point except on long standing, besides which it takes up large quantities of extractive matters and oily bases which completely hide the strychnine when the chloroform is evaporated. The strychnine is separated from this mass by digesting with concentrated sulphuric acid at 100° C. As the strychnine as well as the extractive mass is partly decomposed by this method (*Ber. der Chem. Ges.*, xviii., 3429), it is very unsatisfactory, since when very small amounts of the sample are submitted, the utmost economy in work is necessary.

The following method, modified from the usual methods, has been found by us in every case to yield excellent results. The stomach contents or viscera properly comminuted are weighed, and an aliquot part taken for analysis. The mass is digested in a beaker over night, at a warm temperature, with water acidulated with acetic acid. The contents of the beaker are filtered by pressing through muslin, and then passing through paper. The clear filtrate is evaporated on the water-bath to soft dryness, an excess of ordinary 80 per cent alcohol added, and boiled ten minutes with stirring, and allowed to stand one-half hour at a warm temperature. This extraction is repeated, the alcohol extracts united, filtered, evaporated to soft dryness, and the residue taken up with a little water acidulated with acetic acid, and shaken out with pure acetic ether in a separating funnel. Successive fresh portions of acetic ether are used until the solvent shows by its colour, and by the evaporation of a few drops, that it does not contain extractive matter. As many as twelve extractions are sometimes necessary to accomplish this. Care should be taken in each case to allow time for as complete separation as possible between the two layers. The purified acid aqueous liquid, which need not exceed in bulk 50 c.c., is now returned to the separator, an equal quantity of fresh acetic ether added, and enough sodic carbonate in solution to render the mixture slightly alkaline, and the separator is then thoroughly shaken for several minutes. All the alkaloid should now be in solution in the acetic ether, but a second shaking of the alkaline liquid, with acetic ether, is always made, the two extracts united, and evaporated in a glass dish over hot water to dryness. It will now be found that the residue shows the alkaloid fairly pure, but not pure enough for quantitative results. The residue is dissolved in a few drops of dilute acetic acid, warmed to complete solution, filtered if necessary, diluted to about 30 c.c., and the solution transferred to a small separating funnel; 30 c.c. of ether-chloroform (1-1) are now added, and the separator shaken. After separation the heavier ether-chloroform is allowed to run off, another lot of 30 c.c. of ether-chloroform is added, the separator shaken, and immediately enough ammonia-water added to render the mixture alkaline, and the whole vigorously agitated for several minutes. After separation is complete the ether-chloroform layer is run out into a clean 50 c.c. glass-stoppered burette. The alkaline water solution is agitated with 20 c.c. more of the ether-chloroform, separated, and this extract added to that in the burette. The burette is now supported over a small weighed glass dish, which is kept warm on a water-bath, and the liquid allowed to evaporate gently, drop by drop, until a sufficient quantity of the pure alkaloid has collected in the centre of the dish to render an accurate weighing possible, or else all of the alkaloid may be collected and weighed at once. After all possible tests have been made upon the weighed alkaloid, the remainder is re-dissolved in a drop or two of acetic acid, a little water added, and the dish exposed under a bell-glass to the fumes of ammonia. After standing some time all the strychnine is found crystallised out in the beautiful characteristic needle-formed crystals. The mother-liquor is drawn off with a small fine-pointed tube and rubber bulb, the crystals carefully washed with a little water and dried over sulphuric acid. The glass dish containing these crystals is kept as the final exhibit, and is shown in evidence. Another convenient exhibit may be prepared by moistening a small filter-paper with a solution of the alkaloid in dilute acetic acid, then moistening with a solution of potassium dichromate: this paper on being dried may be kept indefinitely. On moistening it, and touching it at any time with a drop of strong sulphuric acid, a violet film, changing to cherry-red, is formed at the place of contact.

The point which seemed most doubtful in using the above method of analysis was whether, after making the purified extract alkaline and shaking in the separating funnel with acetic ether, the solution of the alkaloid would be complete. Experiments were undertaken to investigate this point, and it appeared that if the alkaloid was precipitated in the presence of the solvent the solution was so complete that no trace of strychnine could be found in the alkaline-water residue, nor could any bitter taste be detected. In order to test the general efficacy of the method, a mixture was made up in the laboratory of starch, glucose, cane sugar, and lard, with 85 per cent of water. Four lots, of about 100 grms. each, were measured out into beakers. Into each of the first two of these was weighed exactly 25 m.grms. of a sample of Merck's strychnine sulphate, which I satisfied myself by careful analysis to have the formula—

$$(C_{21}H_{22}N_2O_2)_2H_2SO_4;\ 5H_2O.$$

Twenty-five m.grms. of this salt were therefore equal to 19·5 m.grms. of the alkaloid. One analysis yielded 19·4 m.grms., the other 19 m.grms., of the alkaloid, an average of 98·4 per cent. Into each of the other two breakers 20 m.grms. of pure strychnine alkaloid was weighed. One analysis yielded 17·6 m.grms., the other 18·6 m.grms., an average of 90·5 per cent.

The next trials were made on a mixture of 200 grms. of meat-hash, 50 grms. sugar, 5 grms. starch, and 500 grms. water. Into this 80 m.grms. of the pure alkaloid, dissolved in a little dilute acetic acid, was thoroughly stirred, and the mixture set away in a warm place for two weeks. At the end of this time the whole mass was weighed, and portions taken for analysis, the analyst being unaware of the amount of strychnine that had been added. The results of the analysis were as follows:—

Total weight of mixture .. .. 753 grms.

I. 216 grms. of mixture gave 20·1 m.grms. strychnine.
II. 287 „ „ „ 25·6 „ „

Calculated for 753 grms. mixture.

	I.	II.	Actually weighed in
M.grm.	70·07	67·17	80
Grains	1·08	1·04	1·23
Per cent recovered ..	87·8	86·2	

As a result of these experiments we are led to believe that the method as described can be depended upon to recover more than 85 per cent of the amount of strychnine present in complex organic mixtures.

The method has been used in working on two separate cases of suspected strychnine poisoning, in both of which the alkaloid was easily detected.

Case A.—The case of a woman who was taken sick directly after drinking a glass of beer, in which poison was supposed to have been put. She was soon after seized with tetanic convulsions, and died within an hour. The stomach was removed within a few hours after death. The total weight of the stomach contents, as submitted to us, was 261·3 grms., or 8·4 fluid ounces; 77·2 grms. taken for analysis yielded 10·1 m.grms. of the

pure alkaloid, equal to 0·53 grain in the whole amount of 8·4 fluid ounces. Another analysis, on 90·7 grms. of the material. yielded 10·4 m.grms., equal to 0·46 grain in the whole amount. The detection of ½ grain of the alkaloid in 8·4 fluid ounces of the stomach contents was in this case a complete substantiation of the diagnosis of death from strychnine poisoning.

Case B.—In this case strychnine had been administered in a glass of whisky, death following in about an hour with convulsions. The stomach was removed the next day. As submitted for examination the stomach contents weighed 643·6 grms., equal to 20·7 fluid ounces. One analysis yielded an amount of the alkaloid equal to 0·66 grain, another an amount equal to 0·71 grain, for the whole sample. The 21·7 fluid ounces of stomach contents contained therefore, at the lowest estimate, 0·66 or ⅔ grain of strychnine alkaloid.

It may be said that in the two cases as described the conditions were unusually simple, death having occurred with well-defined symptoms. No antidotes were used, and no decomposition had taken place in the samples when analysed. If narcotic alkaloids, such as morphine, have been used as antidotes to the strychnine poisoning, or if much decomposition has taken place in the body, with the formation of cadaveric alkaloids, both quantitative and qualitative results may be to some extent interfered with. Morphine, however, on account of its very limited solubility in ether-chloroform, could only appear as traces in the final strychnine residue obtained by this method. Whereas if much decomposition had taken place, the presence of ptomaines would be at least suspected, and the question of the purity of the final residue very carefully considered.

The qualitative examination of the weighed residue as has already been pointed out is divided into three groups, chemical, morphological, and physiological. A minute portion of the residue is dissolved in a drop of strong sulphuric acid and touched with a moist crystal of potassium dichromate; the beautiful purple oxidation product, changing rapidly through crimson to cherry-red, immediately appears. A minute portion of the residue is dissolved in a drop of strong sulphuric acid on platinum foil. If the foil is now connected with the positive pole of a dry cell battery and the drop of acid touched with a platinum wire from the negative pole immediately, the blue oxidation tint will flash out.

A portion of the residue dissolved in dilute acetic acid, the acid evaporated off, this residue taken up with water and exposed to the fumes of ammonia, gives beautiful tufts and silky needle-like crystals of the alkaloid, which can be studied with the microscope. A little of the residue dissolved in a drop of nitric acid gently warmed and touched with a minute particle of potassium chlorate produces an intense scarlet colouration.

If to a dilute acetic acid solution of a portion of the residue a drop of potassium chromate solution is added, beautiful characteristic bush-like crystals and octahedra of the chromate are formed, and can be observed under the microscope. These crystals touched with sulphuric acid give the oxidation test.

Potassium ferro-cyanide and picric acid also give highly characteristic microscopic crystalline forms.

A very small portion dissolved in a dilute acid and further diluted with water has a persistent and distinct bitter taste when a drop of the solution is placed upon the back of the tongue. One part of strychnine in 700,000 parts of water can be detected in this way.

As a final test the physiological effect on a frog is tried: 2·1 m.grms. per kilogrm. weight is the minimum fatal dose for a frog. For an average-sized frog weighing 25 grms., this means the astonishingly small amount of 0·05 m.grm. In our cases 1 m.grm. was dissolved in a drop of acetic acid, about fifteen drops of water added, and something less than one-tenth of this solution injected under the animal's skin right over the spinal column. In both cases, though the amount of strychnine administered was less than 0·1 m.grm., well-developed tetanic convulsions occurred in ten minutes and death in half an hour. —*Transactions of the Academy of Science of St. Louis*, vi., No. 17.

DETECTION OF TRACES OF CHLORINE.

By A. VILLIERS and M. FAYOLLE.

We have lately indicated (*Comptes Rendus*, pp. 1152 and 1204) a procedure for the recognition of hydrochloric acid in presence of hydrobromic and hydriodic acids, founded on the formation of oxidation products by the action of the chlorine liberated by means of potassium permanganate and sulphuric acid upon an acid solution of aniline.

This reaction, on operating as we have proposed, enables us to detect exceedingly minute traces of chlorine. We have, however, observed that the sensitiveness obtained is not constant, and that it is greater or smaller according to the specimen of aniline used in preparing the reagent.

With pure aniline and hydrochloric acid we obtain aniline-black if the chlorine is abundant, but a brown tint, not very decided, if it only exists in traces. With certain commercial anilines, on the contrary, the smallest quantities of chlorine yield a very intense blue colour, turning afterwards to red. We have been led to think that this latter colouration is due to impurities in the aniline, which has induced us to try separately the action of chlorine upon the higher bases, toluidines, and xylidines. These experiments have shown us that the colourations which we may observe with the above reagents presenting the greatest sensitiveness are due to the presence of orthotoluidine in the aniline. If instead of aniline we use orthotoluidine in the preparation of the reagent, we obtain with the chlorides a splendid blue colouration, which becomes a violet-red colouration in heat or in the cold after the lapse of some time.

This reaction is still very distinct even with a quantity of chlorine smaller than 1-10th m.grm. It would hence seem that orthotoluidine might be advantageously substituted for aniline. But the use of this substance presents an inconvenience. The bromised precipitate obtained with the bromides does not remain absolutely colourless, even in the total absence of chlorine, contrary to what occurs on the use of aniline; but it appears to be partially decomposed, and becomes coloured in a decided manner, especially in heat.

It is true that the liquid separated from the precipitate by filtration is almost colourless; still, we may observe a slight tint. In like manner the liquid obtained after treatment with silver nitrate, ammonia, and hydrogen sulphide is not absolutely colourless. We thus see that if the substitution of orthotoluidine for aniline enables us to obtain more intense colourations with the same quantity of chlorine, it may leave some uncertainty in the mind in case of traces of chlorine below 1-10th m.grm.

We may easily remedy this inconvenience by using a reagent containing both aniline and orthotoluidine; say:—

Saturated aqueous solution of colourless aniline	100 c.c.
" " " orthotoluidine ..	20 "
Glacial acetic acid	30 "

In this case if the reagent is in excess (about 5 c.c. to 0·1 grm. of the mixture of the halogens), there is no longer formed bromised toluidine, but bromised aniline, stable and perfectly white in the absence of chlorine; and whether we operate directly or first precipitate in the state of salts of silver and treat with ammonia and sulphuretted hydrogen, we never observe any blue or red colour in the liquid. This reagent gives in a constant manner a very distinct indication of chlorine if the proportion of the latter is 0·1 grm. or even 1-10th m.grm. In the absence of chlorine the result is completely negative.

The limited action of chlorine upon pure orthotoluidine in an acid solution seems to be a simple and expeditious manner of obtaining certain safranines. The violet colouring matters obtained present all the characters of these substances. The addition of concentrated sulphuric acid turns them first to blue and then to green. The latter liquid, on the addition of colour, resumes its primitive colour.

Inversely the action of chlorine on an acid solution of aniline enables us to detect quickly in the latter the presence of orthotoluidine. The addition of a few drops of chlorine water occasions a brown colour if the aniline is pure, but blue and afterwards violet if orthotoluidine is present.—*Comptes Rendus*, cxviii., p. 1413.

ON THE ANALYTICAL SEPARATION OF CHLORINE AND BROMINE.

By R. ENGEL.

Hitherto it has not been practicable to separate chlorine and bromine by means of crystallisation. We were not aware of any substance which, if added to a mixture of chloride and bromide, could liberate exclusively the one or the other of these bodies so that their separation might be effected by solution or distillation.

The difficulties encountered in setting bromine at liberty with the exclusion of chlorine in a mixture of alkaline chlorides and bromides by the action of oxidising agents is explained by the fact that the formation heat of hydrobromic acid in a state of solution (29·5) is included between the formation heats of anhydrous hydrochloric acid (22) and the same acid in the dissolved state (39·3), and that the solutions of hydrochloric acid contain, above a certain concentration varying with the temperature, a quantity of the acid in an anhydrous state.

I have been able to effect the separation of chlorine and bromine in a complete manner by the action of ammonium persulphate. This substance, discovered by M. Berthelot and now met with in commerce in a state of great purity, decomposes the bromides, setting the bromine at liberty, without affecting the chlorides if the solution is sufficiently dilute.

The separation is effected as follows:—We dissolve from 1 grm. to 2 grms. of the mixture of alkaline chloride and bromide in from 150 to 200 c.c. of water, and add to the solution from 3 to 5 grms. of ammonium persulphate. The mixture is heated to 70° or 80°, and a current of air is passed into the liquid which carries away all the bromine. The operation requires about an hour, and the separation is theoretically perfect.

The bromine is collected in a dilute solution of sulphurous acid, and it is determined either in the state of silver bromide or, after destroying the excess of sulphurous acid and neutralising the liquid, by standard silver nitrate, using potassium chromate as indicator.

It is better to collect the bromine in a dilute solution of sulphurous acid rather than in a solution of potassium iodide, because the decomposition of ammonium persulphate by heat liberates oxygen containing traces of ozone or perhaps persulphuric anhydride, according to Berthelot, which react upon potassium iodide. The quantity of iodine liberated in an hour under this influence may reach to 0·006 to 0·007 grm.

If under the conditions indicated above ammonium persulphate is caused to act upon pure commercial sodium chloride, and if the current of air which traverses the solutions is directed into washing bottles containing silver nitrate, we observe after about fifteen minutes a slight turbidity in the nitrate of silver. This turbidity, compared to that produced by sodium chloride in the same volume of silver nitrate, corresponds to some hundredths of m.grm. of the former salt, but I do not believe that it corresponds to one-tenth of a m.grm.

I have not yet been able to decide if this turbidity is due to traces of bromine contained in the chloride, to hydrochloric acid, to chlorine, or to a mixture of these. Their identification in so small a quantity and in presence of ozone or of persulphuric anhydride presents the greatest difficulties. I hope, however, to effect it by means of the sensitive reactions recently discovered by M. Villiers. However it may be, this phenomenon has no influence on the separation and the determination of bromine and chlorine.

Ammonium persulphate may likewise serve for separating the iodine of the iodides in presence of chlorides and bromides. In the cold and in presence of sodium acetate all the iodine of the iodides is precipitated by the persulphate without setting free the smallest trace of bromine or of chlorine. But the iodine cannot be separated by heat, as there is formed, in fact, in heat a certain quantity of iodic acid. We operate therefore in the cold, separating the iodine by means of carbon disulphide, and titrating with sodium thiosulphate.—*Comptes Rendus*, cxviii., p. 1263.

SOIL AND ASH ANALYSIS.—PROVISIONAL METHODS.*

Soil.

Sampling.

The soil selected should be, as far as possible, in its natural condition, not modified by recent applications of manure, or changed by the transporting action of water or wind. Surface accumulations of decaying leaves, &c., should be removed before taking the sample. To eliminate accidental variations in the soil, select specimens from five or six places in the field which seem to be fair averages of the soil, remove 2 or 3 pounds of the soil, taking it down to the depth of 6 to 9 inches, unless there is a change from top soil to subsoil at a less depth, so as to include the whole depth of the soil. Mix these soils intimately, remove any stones, shake out all roots and foreign matters, and dry the soil until it becomes friable. Break down any lumps in a mortar with wooden pestle, but avoid pulverising any mineral fragments; pass 8 to 10 pounds of the soil through a 1 m.m. sieve, rejecting all pebbles and material too coarse to pass through the sieve, noting the percentage amount of soil so rejected. If the amount equals or exceeds 20 per cent this should be pulverised to pass through a 2 m.m. sieve, and in this state submitted to analysis. Once more mix intimately the sifted soil. Expose in thin layers in a warm room till thoroughly air-dry (or dry it in air-bath at temperature of 40°), place 6 to 8 pounds in a clean bottle, with label of locality and date, and cork tightly.

The soil is rapidly dried to arrest nitrification; it is not heated above 40° lest there be dissipation of ammonia compounds, or a change in the solubility of the soil. The normal limit to which the soil may be heated in place by the sun's rays should not be exceeded in preparing a soil for an agricultural chemical analysis.

Hygroscopic Moisture.

Place 5 grms. of air-dry soil in a flat-bottomed and tared platinum dish; heat in air-bath to 110° for eight hours; cool in a desiccator and weigh; repeat the heating, cooling, and weighing at intervals of an hour till constant weight is found, and estimate the hygroscopic moisture by the loss of weight. Weigh rapidly to avoid absorption of moisture from the air.

Water-Holding Power.

In the throat of a clean 3-inch glass funnel place a very small filter, just large enough to prevent the soil from

* Official Methods of Analysis adopted by the Association of Official Agricultural Chemists (American) at its Meeting at Chicago, August, 1893.

running through the stem; wet the filter and add 100 grms. of the air-dry soil; from a graduate containing 100 c.c., pour water on the soil till it is thoroughly wet and a few drops pass through; let it stand undisturbed till no more water flows from the soil, the funnel being covered with a glass plate to prevent evaporation. Return the water which has filtered through to the graduate. The number of c.c. taken up by the soil will show the percentage capacity of the soil to hold water.

In using this process certain precautions are necessary to secure uniform results. The soil should be simply poured into the funnel, and not pressed or compacted in any way. When water is poured upon the soil, no disturbing influence, no handling or shaking of the soil should take place.

Capillary Power of Soils.

This is determined by filling a long glass tube with soil, placing the lower end in water, and marking the height to which the water ascends, as shown by the changed colour of the soil in the tube.

Volatile Matter.

The platinum crucible and 5 grms. of soil used to determine the hygroscopic moisture may be used to determine the volatile matter. Heat the crucible and dry soil to low redness. The heating should be prolonged till all organic material is burned away, but below the temperature at which alkaline chlorides volatilise. Moisten the cold mass with a few drops of a saturated solution of ammonium carbonate, dry, and heat to 150° to expel excess of ammonia. The loss in weight of the dry soil represents organic matter, water of combination, salts of ammonia, &c.

Water-soluble Materials of the Soil.

To prepare a water extract of the soil, a percolator of glass or tin may be employed. It should be large enough to hold one kilo. of soil.

By means of a perforated rubber stopper connect the neck of the percolator with a two-necked bottle of 2 litres capacity, pour sufficient distilled water (ammonia free) on the soil to moisten it all, and let the whole stand undisturbed for half an hour, then add more pure distilled water, and if the filtration is too slow use the filter-pump, till a litre of filtrate is secured. If the soil extract is cloudy, filter through a plain filter.

1. *Soluble Solids.*—Evaporate 100 c.c. to dryness on the water-bath in a tared dish to determine the percentage of water-soluble materials in the soil; each grm. of residue representing 1 per cent of such materials. Test this dry residue for nitrates by pouring over it 10 c.c. of pure H_2SO_4, holding in solution 3 or 4 m.grms. of brucine sulphate.

2. *Chlorides.*—Titrate 100 c.c. with standard decinormal silver nitrate with two drops of a solution of K_2CrO_4 as an indicator. Titrate in a white porcelain dish and view the reaction through a yellow glass plate of such tint as will eliminate the colour of the chromic solution. The reaction will then be sharply defined.

3. *Sulphates.*—Precipitate the sulphates in 100 c.c. of the soil extracted with $BaCl_2$, in presence of a few drops of HCl.

Reserve the rest of the water solution for the estimation of nitrates.

Acid-soluble Materials.

In the following scheme for soil analysis it is recommended to use the air-dry soil from the sample bottle for each separate investigation. A determination made once for all of hygroscopic moisture and of water of combination on a separate specimen of air-dry soil will afford corrections for all the other samples used. It is not desirable to ignite the soil before analysis or to heat it so as to change its chemical properties.

1. *Acid Digestion of the Soil.*—Place 10 grms. of the air-dry soil in a 150 to 200 c.c. Bohemian glass flask, add 100 c.c. of pure HCl of sp. gr. 1·115, insert the stopper, wire it securely, place in a steam-bath, and digest for thirty-six hours at the temperature of boiling-water. Pour the contents of the flask into a small beaker, wash out with distilled water, add the washings to the contents of the beaker, and filter through a washed filter. Residue is the amount insoluble in hydrochloric acid. Add a few drops of HNO_3 to the filtrate, and evaporate to dryness on the water-bath; take up with hot water and a few drops of HCl, and again evaporate to complete dryness. Take up as before, and filter into a litre flask, washing with hot water. Cool and make up to mark. This is solution "A." The residue is soluble silica.

2. *Ferric Oxide, Alumina, and Phosphoric Acid.*—To 100 c.c. or 200 c.c., according to the probable amount of iron present, of the solution A, add NH_4OH to alkaline reaction (avoiding excess), to precipitate ferric and aluminic oxides and phosphates. Expel the excess of ammonia by boiling, allow to settle, decant the clear solution through a filter, add to the flask 50 c.c. of hot distilled water, boil, settle, and decant as before. After pouring off all the clear solution possible, dissolve the residue with a few drops of HCl with heat, and add just enough NH_4HO to precipitate the oxides. Wash by decantation with 50 c.c. of distilled water, and then transfer all the precipitate to the filter and wash with hot distilled water till the filtrate becomes free from chlorides. Save the filtrate and washings, which form solution B. Dry the filter and precipitate at 100°, transfer the precipitate to a tared platinum crucible, burn the filter, and add the ash to the precipitate, heat the whole red hot, cool in desiccator, and weigh. The increase of weight, minus the ash of filter and the phosphoric acid (found in a separate process), represents the weight of the ferric and aluminium oxides.

3. *Ferric Oxide.*—Precipitate 100 c.c. of solution A, as under 2, except that only one precipitation is made; wash with hot water; dissolve while wet in dilute H_2SO_4; reduce with zinc and estimate ferric oxide by a standard solution of potassium permanganate. To prepare the potassium permanganate solution, dissolve 3·156 grms. of pure crystallised potassium permanganate in 1000 c.c. of distilled water, and preserve in a ground-glass stoppered bottle, shielded from the light. Standardise this solution with pure ferrous sulphate or ammonio-ferrous sulphate or oxalic acid.

The weight of ferric oxide deducted from ferric oxide and alumina (12), with corrections for filter-ash and phosphoric acid, will give the weight of alumina in 2 grms. of air-dry soil.

4. *Phosphoric Acid.*—This may be estimated in the above iron solution if the soil is sufficiently rich, by the molybdate method, given under Fertilisers; or if the quantity of soil represented in the iron solution is not sufficient, a fresh portion of solution A may be taken, and the phosphoric acid determined directly by the molybdate method.

5. *Manganese.*—Concentrate the filtrate and washings (solution B) to 200 c.c. or less; add NH_4OH to alkalinity; add bromine water and heat to boiling, keeping beaker covered with watch crystal; as the bromine escapes, the beaker is allowed to cool somewhat, ammonia and bromine water again added, and heated as before.

This process is continued until the manganese is completely precipitated, which requires from thirty to sixty minutes, and the solution filtered while still warm, the precipitate washed, dried, ignited, and weighed; estimate as Mn_3O_4.

6. *Lime.*—If no manganese is precipitated, add to solution B, or the filtrate and washings from 5, 20 c.c. of a strong solution of NH_4Cl and 40 c.c. of saturated solution of $(NH_4)_2C_2O_4$ to completely precipitate all the lime as oxalate, and convert the magnesia into soluble magnesium oxalate. Heat to boiling, and let stand for six hours till the calcium oxalate settles clear, decant the clear solution on a filter, pour 50 c.c. of hot distilled water on the precipitate, and again decant the clear solution on the filter,

transfer the precipitate to the filter, and wash it free from all traces of oxalates and chlorides. Dry, and ignite the precipitate over the blast lamp until it ceases to lose weight, weigh, and estimate as CaO; carefully moisten with H_2SO_4, heat the inclined covered crucible gently to avoid loss, then intensely, and weigh as $CaSO_4$.

7. *Magnesia.*—Concentrate the filtrate and washings (from 6) to 200 c.c., place in a half-litre Erlenmeyer flask, add 30 c.c. of a saturated solution of Na_2HPO_4 and 20 c.c. of concentrated NH_4HO, cork the flask, and shake violently at intervals of a few minutes till crystals form, then set the flask in a cool place for twelve hours. Filter off the clear liquid through a tared Gooch filter, transfer the precipitate to the filter, and wash with dilute ammonium hydrate (1 : 3) till the filtrate is free from phosphates; dry and ignite the crucible, at first gently and then intensely, to form magnesium pyrophosphate. The increase of weight × 0·36024 = MgO. By using an Erlenmeyer flask free from scratches and marks, and shaking violently instead of stirring with a glass rod, the danger is almost entirely avoided of crystals adhering to the sides of the vessel; but if crystals do adhere they are readily removed by a rubber-tipped glass rod.

8. *Sulphuric Acid.*—Evaporate 200 c.c. of solution A (1) nearly to dryness on a water-bath to expel the excess of acid; then add 100 c.c. of distilled water; heat to boiling and add 10 c.c. of a solution of $BaCl_2$, and continue the boiling for five minutes. When the precipitate has settled, pour the clear liquid on a tared Gooch filter, treat the precipitate with 50 c.c. of boiling water, and transfer the precipitate to the filter, and wash with boiling water till the filtrate is free from chlorides. Dry the filter and ignite strongly. The increase in weight is barium sulphate, which multiplied by 0·34331 = SO_3 in 2 grms. of air-dry soil.

9. *Potash and Soda.*—[To another portion of 200 c.c. of solution add $BaCl_2$ in slight excess, and make alkaline with ammonia to precipitate sulphuric and phosphoric acids, ferric oxide, &c. Then precipitate the calcium and barium by ammonium oxalate.*] Evaporate the filtrate and washings to dryness, heat to a low red heat to decompose oxalates and expel ammonia salts, dissolve in 25 c.c. of distilled water, filter and wash the precipitate, add to the filtrate and washings 10 c.c. of baryta water, and digest for an hour. Filter and wash the precipitate, add ammonium carbonate to the filtrate to complete precipitation of baryta, filter and wash this precipitate. Evaporate the filtrate and washings in a tared platinum dish, gently ignite the residue to expel ammonia salts, cool, and weigh. The increase of weight represents the potassium and sodium chloride in 2 grms. of air-dry soil.

Separate and estimate the potassium chloride by platinic chloride according to the method given for potash determination.

Subtract the weight of potassium chloride as thus found from the weight of potassium chloride and sodium chloride. The difference represents sodium chloride.

Alternate Method.—For an alternate method for alkalis, use J. Lawrence Smith's method as given in Crookes's "Select Methods," second edition, pp. 28 to 40.

10. *Other Alkali Metals.*—The salts of lithium, cæsium, and rubidium are occasionally found in very small amounts in soils. The agricultural uses of these salts are still in question, and their amount is too small to admit of quantitative estimation. A quantitative examination may be made by the spectroscope with the water-soluble materials evaporated to dryness and dissolved with 2 or 3 drops of HCl. Test by the spectroscope with a platinum wire in a Bunsen flame.

Nitrogen of the Soil.

The nitrogen compounds in the soil are usually placed in three classes:—

1. The nitrogen combined with oxygen as nitrates or nitrites, existing as soluble salts in the soil.

2. The nitrogen combined with hydrogen as ammonia, or organic nitrogen easily convertible into ammonia. The ammonia may exist as salts, or be occluded by hydrated ferric or aluminium oxides and organic matter in the soil.

3. The inert nitrogen of the soil or the humus nitrogen.

Active Soil Nitrogen.—The material proposed for reducing the nitrates to ammonia, and at the same time to bring ammonia salts and organic nitrogen into a condition for separation by distillation, is sodium amalgam. Liquid sodium amalgam may be readily prepared by placing 100 c.c. of mercury in a flask of half-a-litre capacity, covering the warmed mercury with melted paraffin, and dropping into the flask at short intervals pieces of metallic sodium the size of a large pea (taking care that the violence of the reaction does not project the contents from the flask), till 6·75 grms. of sodium have combined with the mercury. The amalgam contains 0·5 per cent of sodium, and may be preserved indefinitely under the covering of paraffin.

To estimate the active soil nitrogen, weigh 50 grms. of air-dry soil and place it in a clean mortar. Take 200 c.c. of ammonia-free distilled water, rub up the soil with a part of the water to a smooth paste, transfer this to a flask of 1 litre capacity, washing the last traces of the soil into the flask with the rest of the water. Add 25 c.c. of the liquid sodium amalgam, and shake the flask so as to break the sodium amalgam into small globules distributed through the soil. Insert a stopper with a valve, and set aside in a cool place for twenty-four hours. Pour into the flask 50 c.c. of milk of lime, and distil, on a sand-bath, 100 c.c. into a flask containing 20 c.c. of decinormal sulphuric acid, and titrate with decinormal soda solution, using dimethyl orange as indicator. Estimate the nitrogen of the ammonia found as active soil nitrogen.

If the ammonia produced is too small in amount to be readily estimated volumetrically, determine the ammonia by Nesslerising the distillate.

Estimation of Nitrates in the Soil.—When it is desired to estimate separately the nitrates in the soil the following method may be used:—Evaporate 100 c.c. of the soil extract to dryness on the water-bath; dissolve the soluble portion of the residue in 100 c.c. of ammonia-free distilled water, filtering out any insoluble residue, place the solution in a flask, and add 10 c.c. of liquid sodium amalgam, insert stopper with valve, set it aside to digest in a cool place for twenty-four hours, add 50 c.c. of milk of lime, distil, and titrate as in 22, and estimate the nitrogen as N_2O_5.

Nesslerising may be substituted for titration when the amount of nitrates is small.

An approximate estimation of the amount of nitrates will be of value in determining which method of estimation to use. This may be done by evaporating a measured quantity of the soil extract, say 5 c.c., on a porcelain crucible-cover on a steam-bath or radiator, having first dissolved a minute fragment of pure brucine sulphate in the soil extract. When dry, pour over the residue concentrated sulphuric acid, free from nitrates, and observe the colour reactions produced.

If the nitrate (reckoned as KNO_3) left upon evaporating the quantity of water taken does not exceed the two-thousandth part of a m.grm., only a pink colour will be developed by adding the sulphuric acid; with the three-thousandth part of a m.grm. a pink with faint reddish lines; with the four-thousandth part, a reddish colour; with the five-thousandth part, a red colour.

By increasing or diminishing the amount of soil extract evaporated to secure a colour reaction of a certain intensity, an approximate estimate may be made of the amount of nitrates present.

Blank experiments to test the acid and the brucine sulphate will be required before confidence can be placed in such estimations.

Total Nitrogen of Soils.—The total nitrogen of soils may be determined by the usual combustion with soda-

* Note by the Secretary.—The sentences between brackets were inserted to repair an evident omission.

lime, but this process is often unsatisfactory because of the large amount of material required when the organic matter or humus is small in amount.

A modification of the Kjeldahl method is more easy to carry out and gives results equally satisfactory. Place 20 grms. of soil in a Kjeldahl flask, and add 20 c.c. of sulphuric acid (free from ammonia) holding in solution 1 grm. of salicylic acid. (If the soil contains much lime or magnesia in the form of carbonate, enough more sulphuric acid must be added to secure a strongly acid condition of the contents of the flask. Add gradually 2 grms. of zinc dust, shaking the contents of the flask to secure intimate mixture. Place the flask in a sand-bath and heat till the acid boils, and maintain the boiling for ten minutes. Add 1 grm. of mercury and continue the boiling for one hour, adding 10 c.c. of sulphuric acid if the contents of the flask are likely to become solid. Cool the flask and wash out the soluble materials with 200 c.c. of pure water, leaving the heavy earthy materials. Rinse the residue with 100 c.c. of water, and add this to the first washings. Place this soluble acid extract in a litre digestion flask, add 35 c.c. of a solution of potassium sulphide, and shake the flask to secure intimate mixture of the contents. Introduce a few fragments of granulated zinc, pour in 75 c.c. of a saturated solution of caustic soda, connect the flask with a condenser, and distil 150 c.c. into a flask containing 20 c.c. of acid, using the same acid and alkali for titration used in Kjeldahl method under "Fertilisers" (*ante*).

Enter the nitrogen found in this operation as total soil nitrogen.

The difference between the total soil nitrogen and the active soil nitrogen will express the inert nitrogen of the soil.

Carbon Dioxide.

This is determined as under "Ash Analysis"—using 1 to 5 grms.—according to the amount of CO_2 present.

Ash.

Preparation of Ash.

Before combustion the material must be thoroughly cleaned from all foreign matter, especially from adhering soil, wood, bark, roots, &c.

The combustion should be carried on at a comparatively low temperature, never reaching a full red heat, because of the danger of volatilising alkaline chlorides, &c., nor in a strong draft of air, lest the lighter parts of the ash be carried away.

Combustion is best carried on in a flat platinum dish in a muffle.

With substances rich in silica and alkalis it is better to first char the substance. Wash with distilled water to remove soluble salts, then dry and incinerate the residue. Evaporate the watery extract and add this to the rest of the ash.

With substances rich in phosphates, *e.g.*, seeds and animal substances, char the material and remove salts by acetic acid, decant the acetic solution, wash with distilled water, and then complete the combustion. Add the acetic solution and washings to the final ash, evaporate to dryness, and gently ignite the whole to decompose the acetates. In whatever way obtained, the whole of the ash should be pulverised and intimately mixed before analysis.

Analysis of Wood Ashes.

Pass 100 grms. of dry ashes through a wire sieve (of 1 m.m. mesh) to separate materials manifestly foreign, *e.g.*, nails, broken glass and pottery, pebbles, &c., and estimate the per cent of such accidental materials. Pulverise any charcoal and semi-fused portions of ash remaining on the sieve, sift them and mix intimately with the sifted ashes, and preserve in stoppered bottles for analysis.

1. *Moisture.*—Take 5 grms. of the prepared sample in a tared platinum dish and heat to 110° in an air-bath to constant weight.

2. *Carbon.*—Heat this dried ash in a platinum dish till the ash is uniformly greyish white and there is no further loss of weight.

3. *Sand and Silica.*—Place 10 grms. of ignited ash in a 150 c.c. Bohemian flask, glass stoppered, measure out 100 c.c. of HCl (specific gravity 1·115) and pour on the ash cautiously to prevent loss, and when all effervescence has ceased, add the rest of the acid; insert the glass stopper, wire it securely, and place in a steam-bath for two hours; empty the flask into a platinum dish, wash with distilled water, adding the washings to the ash solution, and evaporate the whole to dryness on a water-bath. Add 10 c.c. of dilute HCl and 50 c.c. of distilled water to the contents of the platinum dish, transfer the contents to a filter, wash with distilled water till the last drops of the filtrate are free from chlorides, dry and ignite the precipitate, and filter. If there are no grains of sand (revealed by grittiness when stirred with a glass rod), subtract the ash of the filter from the weight of this residue and estimate the rest as silica. If sand is present, boil the ignited and weighed residue in a strong solution of Na_2CO_3 to dissolve silica, wash by decantation to remove all sodium salts, dry, and weigh the sand. The difference between the weight of sand and silica + sand will give the weight of silica.

The filtrate and washings from sand and silica are made up to 1000 c.c. (solution C) and kept for analysis.

4. *Phosphoric Acid.*—Take 100 to 200 c.c. of solution C and estimate P_2O_5 by the official method.

5. *Carbonic Acid.*—Heat 4 to 5 grms. of ash in a muffle till all charcoal is consumed; cool in a desiccator, transfer 2 grms. to a carbonic-acid apparatus. Estimate the CO_2 in any convenient form of apparatus.

Alternate Method.—By Liebig's potash bulbs. The usual process of absorption by solution of KHO, weighing, &c.

6. *Chlorine.*—Pour out the nitric-acid solution from the CO apparatus upon a filter, wash out the last traces of the solution, pass the soluble matters through the filter and wash the insoluble residue with water acidulated with HNO_3. To this filtrate add solution of $AgNO_3$ to complete precipitation of the chlorides, boil and set aside in a dark place until the precipitate has settled completely, filter through a Gooch crucible, and wash with hot water. Dry at 110°, and weigh the silver chloride.

7. *Alternate Method for Chlorine.*—Boil 10 grms. of ash in 400 c.c. of pure water for half an hour, transfer all to a measuring flask of 500 c.c. capacity, wash the beaker, and add the washings to the flask, cool, make up the volume to 500 c.c. and mix intimately; filter off through a dry filter 100 c.c., add a drop of solution of phenolpthalein, and neutralise with dilute HNO_3 till only a faint pink colour remains, add 2 drops of a strong solution of K_2CrO_4 and titrate with standard decinormal solution of $AgNO_3$ (16·956 grms. $AgNO_3$ to 1000 c.c.). Every cubic centimetre of the standard silver solution equals 0·003546 grm. of chlorine.

The reliability of this method will depend upon the accuracy with which neutralisation by nitric acid has been made. The least trace of free acid or alkaline carbonate will vitiate the results.

8. *Sulphuric Acid.*—Take an aliquot part of solution A and determine as under soils.

9. *Oxide of Iron.*—Take 200 c.c. of the original acid solution, nearly neutralise with ammonia, then add 1 grm. of sodium acetate, and acetic acid in slight excess, boil to precipitate ferric phosphate, filter while hot, and wash the precipitate with boiling distilled water till the filtrate is free from chlorides. Dissolve the precipitate on the filter with dilute H_2SO_4 into a small Erlenmeyer flask, wash the filter, dry and ignite and add the ashes to the acid solution in the flask, reduce the ferric to ferrous salt by zinc or by a coil of magnesium wire till a drop of the solution gives no colour with NH_4CNS. Pour off the solution of ferrous salt into a beaker, rinse the flask and add the rinsings to the beaker, add freshly-boiled distilled

water to make 200 c.c. of the solution, add 2 c.c. of sulphuric acid, heat to 70°, and titrate with standard solution of permanganate, and estimate the iron as ferric oxide.

10. *Manganese.*—If a qualitative test shows the presence of manganese, evaporate the filtrate and washings from iron determination to 200 c.c. or less, and estimate as under soils.

11. *Lime.*—Evaporate the filtrate and washings from ferric phosphate to 100 c.c. To the hot solution add 20 c.c. of concentrated solution of ammonium chloride and 40 c.c. of saturated solution of ammonium oxalate; boil the whole for ten minutes and then let it stand in a warm place for six hours; decant the clear liquid upon a filter, wash the precipitate twice by decantation, then bring the precipitate upon the filter, and wash it free from chlorides and oxalates, testing the washings by silver nitrate. Ignite and estimate as under Soils.

12. *Magnesia.*—Evaporate the filtrate and washings from the calcium oxalate to 200 c.c., pour into a clean and unscratched Erlenmeyer flask of 500 c.c. capacity, add 30 c.c. of strong solution of $(NH_4)_2HPO_4$ and 50 c.c. of strong ammonium hydrate, cork the flask and shake violently at intervals of a few minutes till crystallisation is established, and then set aside for twelve hours in a cold place. If crystals should form on the sides of the flask they are readily detached by a rubber-tipped rod. Filter through a tared Gooch filter, wash the precipitate with ammonium hydrate, diluted with distilled water (1 to 3), till the filtrate is free from phosphates. Dry the precipitate, ignite, at first very gently and then intensely, with blast lamp, to convert $Mg_2NH_4PO_4$ into $Mg_2P_2O_7$. Cool in desiccator and weigh. The increase of weight $\times 0{\cdot}36024 = MgO$, in 2 grms. of air-dry soil.

13. *Estimation of Alkalis.*—Concentrate the filtrate and washings from (8) to 100 c.c., add NH_4HO and $(NH_4)_2C_2O_4$ to complete precipitation of barium and calcium, filter, wash the precipitate, evaporate the filtrate and washings to dryness in a platinum dish, and ignite gently. Add to the residue concentrated solution of oxalate of ammonia, evaporate to dryness, and ignite gently. Dissolve residue in distilled water, filter from insoluble MgO, acidify the filtrate with HCl, and evaporate to dryness in a tared platinum dish and ignite gently. The increase of weight represents the potassium and sodium chlorides. Separate and estimate potassium by $PtCl_4$ in the usual way, and determine the sodium by difference.

The ash of mineral coal contains only a small amount of alkalis and phosphates, but a large amount of insoluble material, clay, &c. The value depends mostly upon the sulphate of lime and phosphate present. They are often decomposed with difficulty. It should be ground to fine powder, and 5 grms. placed in the digestion flask with 50 c.c. of HCl (sp. gr. 1·115), and digested in the steam bath for six hours, and the soluble portion analysed in the usual way.

NOTICES OF BOOKS.

Practical Photo-Micrography. By Andrew Pringle, F.R.M.S. London: Iliffe and Son.

The aim of this book is to give practical instruction in micro-photography, and Mr. Pringle is to be congratulated on having thoroughly carried out the idea he had in view. There is no doubt, as he tells us, that the "personal equation" and misinterpretation of microscopic images tend to lead many observers astray in making drawings, even with the aid of such appliances as a *camera lucida* or a "grapho-prism"; and while by faulty manipulation we may be led into false photographic renderings, still the personal equation, or prejudice is obviated.

The most important consideration in choosing a room for this work is that of freedom from tremor under all conditions; a basement is undoubtedly the most suitable, but very few, we fear, can make use of such an apartment without upsetting the domestic economy of the household.

After a few preliminary remarks the author proceeds to describe minutely the microscope and its parts. Chapter III. describes the complete apparatus, which consists essentially of three parts,—that is, a camera, a microscope, and appliances for illumination. The apparatus can be used either vertically or horizontally, according to the nature of the substance under examination. The camera should be capable of stretching at least 30 inches, and in some cases may be required to stretch as much as 60 inches; and though the negative is not, as a rule, larger than 3 inches diameter, still the size of the camera generally supplied for this work is "half plate,"—that is, 6½ ins. by 4¼ ins. In this chapter there is an excellent illustration (fig. 7), showing what is probably the most elaborate apparatus ever constructed for photo-micrography. It was made mainly to Mr. Pringle's design for the Royal Veterinary College, and it certainly appears to be a most beautiful instrument.

Chapter IV. deals with the important subject of "Objectives" and "Oculars," and photo-micrographers are herein urged to use as low-power glasses as possible, and as high a numerical aperture as is consistent with general good quality in the objective.

Chapter V. is devoted to the condenser; its fittings and use; and in Chapter VI. the various sources of light are discussed. Sunlight is undoubtedly the best illuminant for the micro-photographer, but it is not always available, and requires, moreover, a heliostat to keep the ray in a constant position. On the whole the author recommends the two well-known radiants, the oil-lamp and the lime-light. The lime-light is much more intense and actinic than the oil-lamp, the latter requiring, roughly speaking, about thirty times as much exposure as the former.

Chapter VII. is a most valuable one, giving in detail the actual procedure for making photo-micrographic negatives.

The colours of different objects often give the photo-micrographer a deal of trouble, and to remedy this a number of solutions of different tints are recommended for screening off certain rays.

Several chapters give instructions for the usual operations of photography, such as developing, fixing, toning, &c.; and in the Appendix we find a list, with approximate prices, of all the apparatus mentioned in the book, and a few others besides.

The volume is clearly printed in large type, and very well illustrated, while it is adorned with an attractive binding.

Bulletin of the North Louisiana Experiment Station. Tobacco. By J. G. Lee and W. C. Stubbs. Baton Rouge: Issued by the Bureau of Agriculture, No. 25. 1894.

The results of the year 1893 have, we read, fallen below those of 1892, both in quality and quantity. This is, however, readily accounted for by the very unfavourable weather, which affected alike all the tobacco-growing districts. The experiments tried were of two kinds, viz.:—

1. Variety tests of both bright leaf or chewing tobacco, and cigar leaf or smoking tobacco.
2. Fertiliser tests.

For detailed instances in managing a crop of tobacco, in curing the leaf, &c., the reader is referred to *Bulletin* No. 20, Second Series, published in January, 1893, the one now published only giving a description of the experiments tried.

The fertiliser used on the different varieties, in the first series of tests, was the same throughout, and consisted

of a mixture of nitrate of soda, sulphate of ammonia, dried blood, cotton-seed meal, acid phosphate, and sulphate of potash, at the rate of about 400 lbs. per acre; the highest yield of cured tobacco per acre being 910 lbs. and the lowest 540 lbs., while the yields of the unfertilised plants were respectively 600 lbs. the highest, and 210 lbs. the lowest, showing a very great increase in favour of manure,

In the fertiliser tests only one class of leaf was used, and the proportions of the various constituents of the manure were varied. The results showed that there is not much difference in the yields of different fertilisers, but that nitrogen is needed mostly, phosphate second, and potash third; the best results being obtained with a mixture of 160 lbs. of nitrate of soda, 160 lbs. of acid phosphate, and 60 lbs. of chloride of potassium.

Further experiments were carried out with a view to deciding which is the most favourable soil for tobacco-growing; but owing to unfavourable weather these experiments were not as successful as was hoped: it was, however, shown that North Louisiana can produce large paying crops of the bright or yellow leaf type on her loose sandy soil.

Catalog of "A. L. A." Library. U.S. Bureau of Education. Washington: Government Printing-Office. 1893.

THE first thought that comes into one's head, on looking at this volume, is "Why did they not spell 'Catalog' with a 'K'? This half-and-half so-called spelling reform, which is becoming prevalent in America, is, to our mind, worse than going in boldly for complete phonetic spelling: in that case we should know what to expect, and treat the book accordingly; but when we see these tentative efforts it looks like bad spelling, and is irritating.

This "catalog" gives a list of what is considered by its compilers to be, if not the best, at any rate a very good selection of 5000 volumes for a popular library. The selection was made by a committee, who received the suggestions of about seventy-five librarians and specialists, and the books selected were all presented by the publishers, the whole being exhibited at the Columbian Exhibition.

The "catalog," which is designed to be of practical service in selecting and classifying books, covers a wide field of literature on almost every conceivable subject, and will undoubtedly be of great use in forwarding its proposed object.

L'Aluminium, le Manganese, le Baryum, le Strontium, le Calcium, et le Magnesium. (Aluminium, Manganese, Barium, Strontium, Calcium, and Magnesium.) By ADOLPHE LEJEAL. Paris: J. B. Baillière et fils. 1894.

IT may truly be said that aluminium is more widely distributed about the earth than any other metal, it being the principal constituent of clays, felspars, bauxite, cryolite, &c.,—still, until a few years ago, it was looked upon as a comparative rarity in its metallic state. Of late years, however, great improvements have been introduced in its reduction and manufacture, and, though it is still too dear to come into common use, it is gradually becoming more generally known and appreciated. Excellent cooking utensils are made of aluminium; but the stupidity of the British servant, who will insist on cleaning them with soda, soon puts an end to their career. The volume begins with a short account of the history of aluminium, which was discovered by Wöhler in 1828, followed by a description of the chemical and physical properties both of the metal and of its salts.

Chapter IV. describes the principal minerals containing aluminium, and those from which it is most easily reduced; unfortunately our present knowledge of the metallurgy of aluminium does not enable us to obtain the metal from bauxite, but no doubt Science will before long find out a way.

In Chapter V., on the metallurgy of aluminium, we find a large number of processes described, most prominence being given to that of M. Sainte-Claire Deville. We are somewhat surprised that no mention is made of the work recently done by Mr. Claude Vautin; he has been engaged on aluminium for a considerable time, and has produced some remarkable and valuable results.

A few years ago a good deal was heard of electro-metallurgical processes for producing aluminium: the principal of these are described in Chapter VI. Some very large plants have been laid down in different places on the Continent, that at Froges having engines of 800 horse-power, and two large dynamos, giving 15 volts and 6000 ampères each, besides several smaller ones.

The alloys of aluminium, described in Chapter VII., form an important branch of the subject; a large number are here given, and the character of many of them is shown by excellent plates reproduced from photographs taken under the microscope.

Those who have to work with aluminium have long wanted a good solder; several are given on page 249, but we cannot say without trial how far they may be satisfactory.

The rest of the book is devoted to the history of the earthy and alkaline metals, viz., manganese, barium, strontium, calcium, and magnesium; and terminates with what is rather a rarity in a French publication, viz., an excellent index.

CORRESPONDENCE.

TEST FOR COBALT.

To the Editor of the Chemical News.

SIR,—I have noticed a peculiar reaction between cobalt salts and thiosulphates, and would be glad to know whether any of your readers can explain its nature. When a crystal of sodium thiosulphate is added to a little cobalt chloride solution, a deep greenish blue colour is produced. The substance is also formed by fusing hydrated cobalt chloride with crystals of sodium thiosulphate or with anhydrous thiosulphate. It is a greenish blue liquid, which on standing at 60° C. solidifies to an opaque mass. Crystals may be obtained from this by washing repeatedly with strong alcohol or acetic acid, also by adding a little HCl and allowing it to drain off rapidly; they are also produced when the mass is crushed before it has quite solidified.

The substance has a greenish blue colour like that known as "peacock-green," quite different from the colour of cobalt glass. The crystals are semi-transparent, and have a cubical appearance.

Water decomposes the substance, sometimes giving a black precipitate of cobalt sulphide, and at other times a pink solution; addition of sodium thiosulphate revives the colour.

Hydrochloric acid does not decompose it for some time; even after several hours it is not completely destroyed, but the liquid becomes clear again on addition of water. It is very slightly soluble in alcohol and glycerin, insoluble in benzene, nitrobenzene, chloroform, and other solvents.

When hydrated cobalt chloride is dissolved in alcohol and a crystal or two of sodium thiosulphate added, they immediately become peacock-green and melt to a thick liquid, from which small crystals may be obtained. The alcohol is immediately decolourised.

Hydrogen dioxide decomposes it with formation of a dark yellow precipitate and evolution of gas.

Solutions of ammonia, ammonium sulphide, hydrogen sulphide, &c., decompose it.

Sulphuric acid decomposes the substance with evolution of H_2S.

Nitric acid evolves sulphur dioxide, and precipitates sulphur and a dark coloured body containing cobalt and sulphur.

That the test is a very delicate one for cobalt salts may be shown in the following way:—Add one drop of cobalt solution of the ordinary strength to about 20 c.c. of water, drop a piece of anhydrous thiosulphate into a test-tube, and pour a little of the dilute solution upon it; on heating a green colour will be produced. It may also be shown by placing a crystal or two of sodium thiosulphate on a porcelain plate, adding a few drops of the dilute cobalt solution, and allowing the flame of a Bunsen burner to heat it for a few seconds, when the crystals become bluish green.

The reactions take place in presence of nickel, iron, manganese, &c. Acetic acid ("glacial") dissolves the substance on warming, but on heating more strongly decompose it.—I am, &c.,

W. Ball.

Reddish, near Manchester,
July 13, 1894.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. xi.-xii., No. 12.

Telegrams expressing the sentiments of the senders on occasion of the anniversary of the death of Lavoisier have been received from the Roumanian Society of the Physical Sciences and from the Chemical Section of the Imperial Society of the Friends of Natural Science of Moscow.

The proposal to erect a statue in honour of Lavoisier as the founder of modern chemistry has been favourably received by the Academy and by the Chemical Society of Paris.

M. Bayer has isolated from French bauxite a group of elements, vanadium, chromium, molybdenum, tungsten, arsenic, and a new element the reactions of which he wishes to submit to the Society. Its sulphide dissolves in sulphuretted hydrogen, forming a red liquid. Its spectrum presents two rays which appear characteristic. Its proportion in bauxite is very slight, a million kilos. containing only about 2 grms.

Detection of Hydrochloric Acid.—A. Villiers and M. Fayolle.—Already noticed.

Determination of Iodine.—A. Villiers and M. Fayolle.—Already noticed.

On Certain Hydrated Metallic Chlorides.—Paul Sabatier.—The author compares his results with those obtained by Lescœur, which agree only in part.

Action of Methylene Chlorobromide upon Ammonia Dissolved in Methylic Alcohol.—E. Delépine.—It results from these experiments that methylene chlorobromide, a substance perfectly definite from a molecular point of view, leads, whether in heat or in cold, by the action of ammonia dissolved in methylic alcohol, to the base in C_6, the same which ammonia yields when acting upon formal or methylic aldehyd.

Action of Methylene Chloride upon Ammonia in Alcoholic Solution.—M. Delépine.—Methylene chloride, CH_2Cl_2, has been placed in contact with ammonia both in cold and heat. In the cold, after the lapse of six months, there were formed merely insignificant quantities of hexamethylene-amine. In heat the action to be complete required more than eight hours at 100°.

Preparation of Hexachlorophenol.—E. Barral.—The author names this hexachlorophenol, melting at 107°, hexachlorophenol *a*, to distinguish it from that which melts at 46°. By continuing to pass chlorine until there is no further increase of weight, he has obtained white crystals formed of a mixture of several octochlorophenols, C_6Cl_8O, which will form the subject of a future communication.

Thermic Study of the Nitrobenzoic Acids. Influence of Isomerism. Influence of Nitro-substitution.—M. Masnol.—The author determines the solution heats of the nitrobenzoic acids of the anhydrous sodium salts and the formation heats of the salts in the solid state. The numbers formed, compared to the formation heat of sodium benzoate + 17·4 cal. show the influence of the group (NO_2) if substituted for an atom of hydrogen in the mol. It increases the total acidity to the same degree as chlorine, bromine, or oxygen. The comparison of the formation heats of the three salts of sodium shows the variation resulting from the relative position of the group NO_2 with reference to the carbazol. The total quantity of heat liberated decreases as the group NO_2 removes from the acid hydrogen acid.

Preparation of the Acetylgallic and Acetyldibromogallic Acids, and the Determination of the Acetyl in these Combinations.—Paul Sisley.—This lengthy paper does not admit of useful abstraction and is not of sufficient importance for insertion in full.

Total Energy brought into Play in the Organism by the Combustion of the Albumenoids.—C. Matignon.—In order to obtain 1 mol. of uric acid or 2 mols. of urea it is necessary to burn 337 grms. albumenoid. Uric acid seems not to be derived solely from the incomplete oxidation of the albumenoids. It may be produced synthetically within the organism.

The Hydrate of Uric Acid.—C. Matignon.—Uric acid is deposited from its dilute saline solutions in the form of a hydrate, probably $C_5O_3N_4H_4{}_2H_2O$, which is slowly transformed into crystalline uric anhydride.

Metallic Derivatives of Formyl-urea, of Acetyl-urea, and of Oxaluric Acid.—C. Matignon.—The examination of formyl-urea, acetyl-urea, and oxaluric acid seems to indicate that these substances are capable of yielding metallic derivatives by the replacement of the group NH placed between the two negative radicles CO. The author has prepared several such derivatives.

On some Novel Salts of Urea.—C. Matignon.—The author has obtained the acetate, amido-acetate, acid malonate, and glycolate. All these salts, which contain no water of crystallisation and are in general well crystallised, decompose into these constituents, acid and urea, when dissolved in a sufficient quantity of water. The formation of the corresponding ureides by direct dehydration does not succeed with urea acetate and amido-acetate, which would correspond to a considerable absorption of heat. With urea malonate and glycolate the reaction would be notably exothermic.

MISCELLANEOUS.

A Relation between the Atomic Weights. — Mr. Ewart Matthewman, of Huddersfield, writing in the *English Mechanic*, holds that "the *absolute* atomic weights must be whole multiples of a unit, and that the only natural way for these atomic weights to progress is by increments of unity." He takes the atomic weight of oxygen =7, and assigns the following numbers to the elements:—Li, 3; Be, 4; C, 5; N, 6; O, 7; F, 8; an unknown element, 9; Na, 10; magnesium, 11; &c. The difficulty is, of course, to make these figures agree with the atomic weights as determined by actual experiment, which they are very far from doing.

Filter-paper containing Nitro-cellulose. — E. Cramer (*Zeitschrift fur Angewandte Chemie*).—Everyone engaged in analytical work encounters the difficulty that the incinerations of filters with many precipitates take place only slowly, and with others only by the use of ammonium nitrate. This difficulty may be avoided if the cellulose used in the manufacture of the filter-paper is entirely or only partially nitrised. It is simpler to make filter-paper of a mixture of cellulose and nitro-cellulose. Filter-paper containing nitro-cellulose filters more rapidly than ordinary paper, as nitro-cellulose has no tendency to felt up. The incineration of pure nitro-cellulose filters is instantaneous, whence filters made of a mixture of cellulose and nitro-cellulose are preferable for analytical work. The advantages of such filter-papers are the following: — Nitro-cellulose which has already been used for filtration is thus brought into a convenient form in the state of paper. The speed of combustion can be regulated by adding cellulose to nitro-cellulose. The felting of such paper is very small, and the nitro-cellulosic paper is less hygroscopic. [Is the nitro-cellulosic paper equal or superior to ordinary filter-paper in keeping back precipitates, *e. g.*, barium sulphate?—*Ed.* C. N.]

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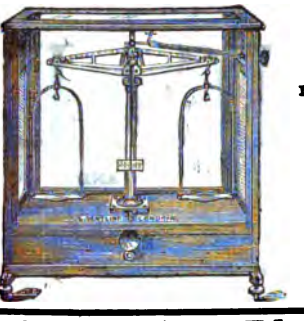

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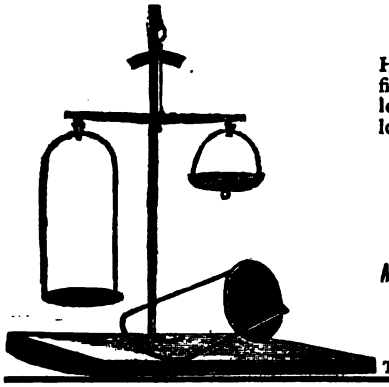

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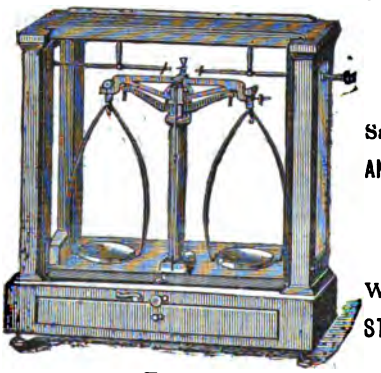

FIG. 3a.

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THE CHEMICAL NEWS.

Vol. LXX., No. 1809.

TECHNICAL EDUCATION.

When even Germany considers that her arrangements for higher education are not incapable of amendment, it is not surprising that we in England should feel moved to revise our position.

Accordingly there has been formed in London a "Technical Education Board," selected, it appears, out of the London County Council. This Board is fully convinced that in the interest of our manufactures "something must be done," and is anxiously considering what that "something" should be. Among other steps a series of "trade conferences" have been held for the discussion of the subject in reference to the various London industries at the County Council Hall. At the last of these gatherings, for the consideration of the "clothing, leather, chemical, and miscellaneous trades," we were, by the courtesy of the Secretary, enabled to be present. The body of the Hall, it appeared, had been set apart for delegates from Trade Associations. This seemed to us not unlike a gathering of the patients at some great hospital to consult as to the modes of treatment to be adopted. Trade associations in England seem to have generally concentrated their attention on the points in dispute between employers and employed, and to have very generally eschewed the development of their respective industries and the means of withstanding alien competition. A few of the speakers had, indeed, visited foreign countries, and had noted the facilities there afforded for technical culture. A question incidentally raised was whether the study of principles of theory should be taken before routine practice in the workshop or afterwards? This question is still under debate in Germany and Switzerland. A return to the old system of apprenticeship was suggested. Other speakers felt that in view of modern industrial organisation this was scarcely practicable. Several speakers seemed to expect little benefit from the training obtainable at technical schools, and wished to adhere to the "practical" career of the workshop, in other words to rule of thumb—the very system which has caused us to be outstripped by some other countries. Germany, it must be remembered, owes her success in certain arts and manufactures chiefly to the greater attention she has paid to theory. At the same time we must urge that as regards the rank and file of the "industrial army," Germany has little advantage over Britain. Her superiority, where it exists, lies in the higher training of the foremen, managers, and, if we may venture to say so, of the employers also. The heads of the great German manufactories of coal-tar colours are not mere capitalists.

The able opening discourse of the Chairman, Mr. Sidney Webb, L.C.C., led us to expect that no inconsiderable attention would be paid to chemical manufactures, a department where scientific principles are of the highest importance, and where mere rule of thumb is hopeless and helpless. He protested against crude theories, but he called attention to the fact that the applications of chemistry in the arts were advancing by "leaps and bounds," and that if we would hold our own we must take the tide at the flood.

But, alas, the chemical arts were at the meeting crowded out. The boot and shoe makers, the wheelwrights, and the tailors were in great force, and had so much to say that at 9.45 no chemical art had been even mentioned, save that a representative of the leather sellers pointed out that in leather-dyeing we were not on a level with the French.

Of course where the trades discussed were so many and so various, no general conclusions could be reached. The trade of the boot maker, the tailor, &c., may possibly be learned to perfection in the workshop alone; but the wheelwright will certainly be aided and improved by a knowledge of geometry and mechanics. The baker should not be entirely ignorant of chemistry and bacteriology, seeing that his trade is based upon the process of fermentation. But this point received scanty notice, and a reference to the anti-hygienic characters of the subterranean bake-houses of London seemed likely to raise unfriendly feelings, and was not enlarged upon.

We submit that the chemical arts, so varied in their character and so widely different in conditions from the other arts mentioned in the prospectus, might well have deserved an evening to themselves, or should at any rate have had the foremost place at the meeting on the 18th instant. They include, besides the manufacture of coal-tar and other colours, the arts of the tanner, soap boiler, varnish and printing-ink maker, and not a few others.

We hope that the efforts of the Technical Education Board will not be relaxed, and that they may meet with every success. We trust that each art will be discussed not from the master's point of view,—as it was said at the meeting,—nor from the workman's point of view, but from the nation's point of view. If the courses of education in elementary public schools—whether Board or denominational—are prolonged and extended, we hope that the cardinal errors of these establishments will be avoided.

GERMAN LAW CONCERNING THE POLLUTION OF RIVERS.

According to the *Zeitschrift fur Angewandte Chemie* (July 1st, 1894), a new law is projected which is not unquestionable both as regards its provisions and the experts who are to decide on its execution.

The object of utilising the water-courses in husbandry, and in obtaining water-power with especial reference to the demands of hygiene of fisheries, is to be secured by very stringent measures. Procedures of expropriation will not only be extensively adopted, but every riparian inhabitant may be compelled to take part in a new project, and to guarantee the result with his property as soon as a high "prospective advantage" is assumed by some adventurous neighbours.

Installations which have been already sanctioned, and which have existed for a long time, may be done away with without compensation. It is thus possible that a chemical work which has for years, on the basis of an official concession, discharged waste waters into a river, may be deprived of this right if—*in the opinion of an authority*—the public interest requires such a restriction. Such a measure may, of course, involve the closure of the establishment.

As the provisions contemplated are so sweeping, the character of the authorities becomes of the greater importance. At the head stands the Upper President, to whom is assigned as Assessor the Medical Board. There is also a "water bureau," and a water-police office, to which is appended as Assessor an official of the governmental engineering department. As assessors we find, therefore, merely physicians or engineers, but, strange to say, no chemists

The prescriptions for the purity of the water are:—

It is prohibited to discharge or introduce into waters, whether subterraneous or superficial:—

a. Substances of such a nature that their introduction may give rise to an infectious disease.

b. Substances of such nature, or in such quantities, that their introduction may involve an injurious pollution of the water or the air, or a decided annoyance to the public.

The Head-President of the province has to determine *what substances and what quantities* are involved in this prohibition. If therefore, *e.g.*, a medical board should assume—perhaps on the basis of a new hypothesis—that the waste water of sugar-works may be dangerous to health or offensive to the public, the Head-President can generally forbid their discharge into the rivers.

The contention that everything should be forbidden which *may* become dangerous is not acceptable. That only should be prohibited which, according to probability and experience, is dangerous.

There is in nature no water which is chemically pure. Surface drainage contains the most varied impurities. It must be remembered that the water from fields manured with night-soil may convey morbific germs into the nearest water-course. The water from laundries and baths must convey numberless toxic micro-organisms into the brooks and rivers, all of which are therefore impure and suspicious.

"Whether a water is or is not technically pure can be decided only on consideration of its intended uses. Whether waste water can be safely discharged into a river must be determined in each case by real experts after consideration of all the attending circumstances. But for industrial waste waters only the technical chemist, not the medical board, can be regarded as an efficient expert. For town-sewage the chemical condition must be decided by chemists, whilst the morbific micro-organisms may be adjudicated by the medical board, and the construction of the sewers by the engineer."

(It will be seen that the principles laid down by our contemporary entirely coincide with the views which have been repeatedly advocated in the Chemical News.)

THE "FLASH POINT" OF OILS FOR BURNING.

We were formerly of opinion that accidents in the use of mineral oils were due to pure carelessness, or to such errors as replenishing the lamp while burning, allowing the gallery or the wick-holder to become foul and clogged, &c. Hence we felt no scruple in using a petroleum lamp as the best light for microscope work. But we were staggered by the regretted death of Prof. Wroblewski, one of the most careful and judicious experimentators in the world. This *savant* had been accustomed to the nicest and most critical work, yet, in spite of all his skill, he was burnt to death in consequence of the overturning of a petroleum lamp. Since then the increasing use of petroleum and paraffin lamps has paved the way to a number of serious, and even fatal, accidents, and has given room to a feeling that additional precaution is necessary in the use and storage of mineral oils.

The British legal standard is a flash point of Abel's apparatus at 73°. It will be at once felt that this standard is too low if we consider that in 1893, from April to September, there were in London twenty days in which the temperature in the shade was 80° to 90° F., and three days when it ranged from 90° to 100° F.

Hence our present national standard is far too low, and should be raised to 100° or 105°. The Scottish and the Manchester Sections of the Society of Chemical Industry, and several Chambers of Commerce in Britain, have passed resolutions to the effect that the minimum legal standard should be 100°.

The standard flash point in Canada is 95°; in the United States of America it is 100° F.; and some of the States have recently demanded a higher standard. The standard adopted by the German Government is said to be 69·8° F. (?).

It is worthy of notice that our late friend Dr. Young, F.R.S., was strongly of opinion that the minimum flash point should be fixed at 100° to 105°. As he was the creator of the British mineral oil industry, his opinion seems to us entitled to great weight.

A Committee, having its seat at the New Club, Glasgow, has been formed to diffuse information on this important subject.

ON THE DETERMINATION OF BARIUM SULPHATE.

By M. RIPPER.

The author avoids the error due to the reducing action of the carbon of the filter by the following treatment of the precipitate:—

The washed filter containing the barium sulphate is introduced moist into a platinum crucible, carbonised and incinerated with the cover on. So much bromine water is then added to the contents of the crucible that no further decolouration takes place, which generally requires from 5 to 8 drops of bromine water. A small excess of this oxidising agent and from 10 to 15 c.c. of distilled water are added, and the crucible is heated on the steam-bath until all the bromine is expelled, which requires only a few minutes.

After the complete expulsion of the bromine from 2 to 3 drops of hydrochloric acid are added, and the crucible is heated for ten minutes. In no case was the slightest trace of sulphuretted hydrogen perceptible on the addition of the acid. Finally, the acid liquid was decanted off through a small filter, the precipitate on the filter was washed by decantation with hot water three or four times, the small washed filter was returned to the crucible, dried, incinerated, a drop of bromine water or of dilute sulphuric acid added, ignited, and weighed.

The reduction of the barium sulphate can be easily avoided if the precipitate is collected on an asbestos filter in a Gooch crucible. Here, however, Ripper encountered various difficulties. He did not succeed in bringing the crucible filled with asbestos to a sufficiently constant weight either alone or after treatment with dilute hydrochloric acid. Further, the barium sulphate adhered so firmly to the asbestos that the cleansing of the precipitate with hydrochloric acid was rendered very difficult.

These results of Ripper disagree with the statements of E. F. Mar (*Zeit. Anal. Chemie*), and J. J. Phinney (*Amer. Journ. Sci.*), who have both determined barium sulphate by means of the Gooch crucible. Phinney's communications show that a crucible filled with asbestos according to Gooch's directions may be ignited, and the contents treated with hydrochloric acid, without the slightest loss of weight.

The barium sulphate collected in the Gooch crucible can be treated with acids without difficulty. Large quantities of the precipitate can be both distributed in the crucible with a glass rod after moistening, and be easily removed from the crucible, and, after treatment with acid, collected again on the same filter.

Barium sulphate obtained by precipitating a solution of barium chloride, with an excess of sulphuric acid in presence of alkaline chlorides or potassium chlorate, always contains considerable quantities of impurities. Phinney attempted to purify such precipitates by treatment with hydrochloric acid in presence of a sufficiency of sulphuric acid (5 per cent of the vol. of liquid), in order to prevent a simultaneous solution of barium sulphate. Here, however, even in the most favourable case, only from 70 to 90 per cent of the impurities were removed. Equally unsuccessful was a complete purification of the barium sulphate by moistening it after ignition with hydrochloric acid, evaporation to dryness, and extraction with water.

To obtain such a barium sulphate pure, it must be either, according to R. Fresenius, fused with sodium car-

bonate, the melt extracted with water, and baryta re-precipitated as sulphate,—or the impure precipitate is dissolved in concentrated sulphuric acid, and the solution evaporated according to Mar's directions.

As Mar has shown, in his work above referred to, baryta may be completely separated as sulphate, even in presence of large quantities of hydrochloric acid, if sulphuric acid is present in sufficient excess. According to the experiments of E. Browning (*Amer. Journ. Sci.*, xlv., 399), even large quantities of nitric acid and aqua-regia (up to 10 per cent of the vol. of the liquid) do not interfere with the perfect separation of baryta in presence of an excess of sulphuric acid, the precipitate being allowed to stand for six hours. The barium sulphate thus obtained is coarsely crystalline in texture.—*Zeit. f. Anorganische Chemie.*

LONDON WATER SUPPLY.

Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending June 30th, 1894.

By WILLIAM CROOKES, F.R.S.,
and
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford.

To Major-General A. De Courcy Scott, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, July 10th, 1894.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from June 1st to June 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 182 samples examined one was recorded as "clear, but dull," the remainder being clear, bright, and well filtered.

During the month of June, the rainfall at Oxford, representing the mean fall in the Thames valley, has shown an excess of 0·58 inch—the only important excess since July, 1893,—in which month there was an excessive rainfall, the quantity above the 25 years' mean being 1·12 inch. The only other similar instances since then were in October, 1893, when there was a surplus of 0·09, and in March, 1894, when the excess was 0·08 inch. There is this peculiarity in the rainfall of the present June: Of the 2·79 inches of rain that fell, 2·56 came down during the first half of the month—as much as 0·99 falling on one day, the 4th—whilst only 0·23 inch fell during the second half of the month.

The quality of the Thames-derived waters has remained excellent during the month of June. The analytical results are practically identical with those of the previous month, and also with those for June, 1893, the differences being in most instances confined to the third place of decimals; each unit in that position representing one part of extraneous matter in 70,000,000 parts of pure water; a fraction which, translated into units of length, is equivalent to about six yards in the distance between the earth and the moon—a wholly negligible quantity.

We wish to take this opportunity of drawing attention to an improvement in the brown solution used in the colour-meter, by means of which the tint of the different samples of water is ascertained. Some years ago it was found that the liquid originally employed—a solution of ferric chloride and cobalt chloride—was not stable, but gradually changed its standard after use. We instituted many experiments with the object of preparing a liquid of the required tint which would not change on keeping, and for the last two years we have been testing one composed of 0·05 grm. of potassium bichromate and 1·0 grm. of anhydrous cobalt sulphate, dissolved in distilled water, and made up to the bulk of one litre. This brown liquid is of the exact colour and standard of the old brown solution, and it has the advantage of not altering in tint if evaporation is guarded against.

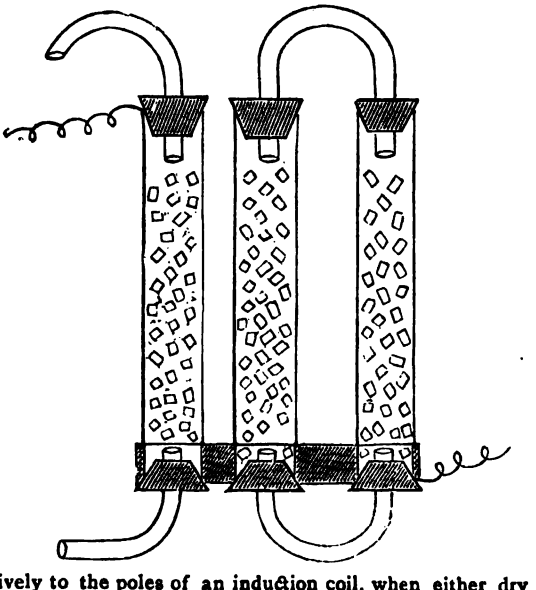
As many engineers and chemists connected with water-works are in the habit of using our colour-meter, and have some difficulty in getting the brown solution of the correct standard, we shall always be pleased to supply some of the properly standardised solution to any one interested in the examination of water.

We are, Sir,
Your obedient Servants,
William Crookes.
William Odling.

AN IMPROVED FORM OF OZONISING APPARATUS.

By H. N. WARREN, Research Analyst.

The apparatus hitherto so much in use and devised by Siemens, which in its simplest form consists of two tubes, the one so much smaller in dimension than the other that when placed inside it a small space is left between the two. The inside of the inner tube, and the outside of the outer tube, are coated with tin-foil and connected respectively to the poles of an induction coil, when either dry air or oxygen is passed through the space between the tubes while the coil is in action.



From careful observations it will be observed that the silent discharge produces over 50 per cent more of ozone than does the disruptive discharge; whereas a silent discharge is never wholly obtained when using any of the general forms of apparatus.

The apparatus which the author has now the pleasure of introducing to the scientific world, shown in the accompanying diagram, consists of two or more tubes of ordinary white glass about three feet long and half-an-inch in diameter, connected together by the aid of corks and smaller tubing. The interior of each tube has to its surface attached small squares of tin-foil (chemically prepared) arranged in close proximity to each other in diamond fashion, similar to what is known as the diamond Leyden jar. The extremities of the tubes being furnished with tubulures to allow of directing a stream of gas when desired through the interior of the apparatus, while the last squares of tin-foil of the first tube are connected to those in the second by strips of foil passing from the interior of the one tube and connected to the interior of the other, thus rendering the whole apparatus, as far as surface is concerned, one continuous length. At the same time, the exterior portion is connected to the poles of a powerful induction coil of special construction, the which has already appeared upon the pages of this journal.

The action of the apparatus was first observed by transmitting a current of air through the same whilst the coil was in action. The gas thus evolved was of a most oppressive odour, but when perfectly pure oxygen was used the contraction in several cases amounted to one-eighth of its original bulk; whereas, in the former experiments, one-twelfth has been about the usual amount observed. The odour in this case resembled that of chlorine, and instantly corroded indiarubber and many other such-like organic substances; while a strong solution of indigo was immediately rendered colourless, many mineral and other oils being perfectly bleached. Experiments are now being performed, such as the bleaching of pepper, &c. The length of spark from the machine employed amounted to 6 inches in length and was of high tension.

Everton Research Laboratory,
18, Albion Street, Everton, Liverpool.

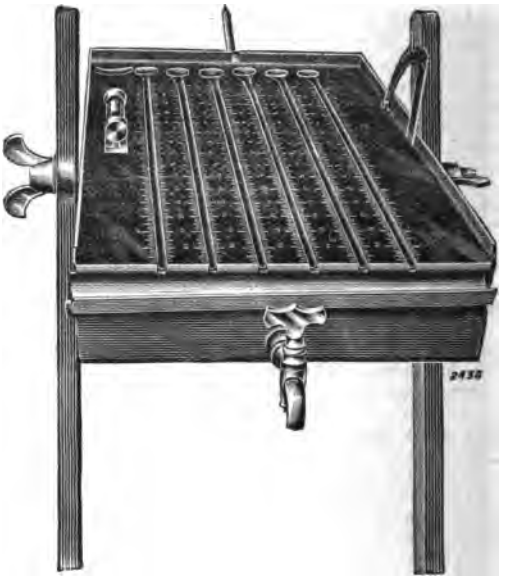
A RAPID METHOD OF ASCERTAINING THE DEGREE OF FLUIDITY OF LUBRICATING OILS AT VARIOUS TEMPERATURES.

By F. W. DAW, Assoc. R.C.Sc.

Mineral oils, either alone or mixed with fatty oils, are now very generally used for all kinds of lubrication. The oils vary greatly in fluidity, from the almost solid hydrocarbon, such as vaseline, to the thin fractions of petroleum, such as kerosene, and it becomes very necessary in selecting these oils for specific kinds of economic lubrication that the fluidity is suitable at the temperature and pressure of working; the mere look of the oils at the ordinary temperature is no criterion of what the fluidity would be at the working temperature of the bearings.

In most large engineering establishments, such as the works of the railway companies, oils are bought by tender, and samples are sent with the quotations. Before any tender is accepted, the oils are examined by the company's chemists as to quality and physical condition. The great length of time necessary to conduct an exhaustive examination of several oils often renders the analysis of little use when, as is often the case, oils are wanted quickly, and contracts are made before the various tests are completed. The writer has been experimenting with a new form of instrument, the "Fluidimeter," recently invented by Mr. H. Joshua Phillips, F.I.C., F.C.S., by which the fluidity or viscosity of several oils at a time can be very quickly determined. Accompanying is an engraving of the instrument, kindly lent for the article by the Editor of *Engineering*.

The engraving was taken from a photograph of the experimental instrument. The perfected fluidimeter consists of a copper bath 14 inches long, 9 inches wide, and about 1½ inches deep, and at the top end there are two holes, one for a thermometer and another for pouring in water or other liquid to be maintained at definite temperatures by a small flame under the bath. The surface of the bath contains six cups connected to the bottom by gutters, all of definite capacity. (The instrument can be made with one cup and gutter or any number). The cups hold 1½ c.c., are 1 inch wide and $\frac{3}{16}$th inch deep, and the gutters are $\frac{1}{16}$th inch wide and $\frac{1}{16}$th inch deep, and are graduated from about 1 inch from the cups in ½ inch to 10 inches near the bottom of the plate. There is a glass plate provided for covering the bath to keep away air currents, and there is a receptacle at the bottom of the bath for receiving the oils as they flow down, and also a tap for letting out the liquid from the bath when required. A protractor of 6 inches radius and divided into single degrees is fixed to the side of the instrument by means of which the bath can be tilted to any desired angle. The surface of the bath is silver plated, and the whole swing upon elevated bearings from two studs fixed in the sides regulated by thumb-screws. The method of testing is as follows:—



Water or oil having been run into the bath at any desired temperature, a small Bunsen flame is placed under the bath, regulated so as to maintain it at the same temperature. The oils to be tested are poured into test-tubes provided with pipettes, and heated in a bath of water or oil until the desired temperature is attained. The bath is now tilted at an angle of 2½° from the horizontal, from the operator, and the oils run into the cups until they reach the zero mark on the scale about an inch from the cups. The glass plate, previously warmed to about the same temperature as the oils, is now slid on, and the bath tilted at any desired angle to the operator, and the time noted that the oils take to reach the 10 inch mark. I find that the time of flow of the oils is practically inversely proportional to the angle of inclination, provided the angle is sufficiently great, or the temperature sufficiently high, to allow the oils to run quick enough to minimise errors due to oxidation or cooling of the oil by air currents. This seeming deviation from the laws of gravitation is, of course, due to the decrease of acceleration consequent upon the loss of "head" and gradual loss in weight of the oil as it flows to the terminus. For instance, the following results were obtained with pure rape oil at a temperature of 180° F.:—

Angle.	Distance.	Time in secs.
2½°	10 inches	33
5°	,,	16
10°	,,	8

A sample of mineral engine oil gave :—

		100° F.	140° F.	180° F.
2½°	10 inches	160	60	28
5°	,,	79	30	14

From these results it would appear that the time of flow could be calculated for any desired angle from one determination at a definite angle. The following results were obtained in comparing the viscosity of pure rape oil at different temperatures with Redwood's viscosimeter, assuming the rate of flow to be 1 at 180° F. :—

At—	Phillips's Fluidimeter.	Redwood's Viscosimeter.
180° F.	1·00	1·00
140° F.	1·59	1·56
100° F.	3·19	3·14
60° F.	7·50	7·37

The great advantage the writer has found in using the instrument is that in cases where several oils have to be examined and to be compared with a standard, a great saving of time is effected, inasmuch as all oils that do not approach the standard in fluidity can be discarded, and an exhaustive examination made only of the oils that agree in fluidity with the standard.

The sole makers of the instrument are Messrs. Townson and Mercer, of 89, Bishopsgate Street, London, E.C.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 21st, 1894.

Dr. ARMSTRONG, President, in the Chair.

MR. E. F. HARRISON was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Alexander Cameron, 13, Stonenest Street, Tollington Park, N.; Charles A. Fogg, 48, Kent Street, Bolton.

Of the following papers those marked * were read :—

*31. "*A Specimen of Early Scottish Iron.*" By MARGARET D. DOUGAL.

The specimen was found on the site of the Fasagh bloomeries, on the north-east shore of Loch Maree, Rossshire—the neighbourhood where the manufacture of iron in Scotland appears to have had its rise nearly three centuries ago. Full particulars of the mechanical characters, determined by Professor Unwin in the engineering laboratory of the Central Institution, are given in the paper, as well as the details of the chemical analysis. Its chemical composition was C=0·192; Si=0·077; S=0·012; P=0·087; Mn = 0·038; Ti = 0·002; Te = 99·770; total = 100·178. From a report by Mr. Ames, the art-metal worker, the metal was of excellent quality, resembling the famous Swedish iron used by the English smiths of the Seventeenth and Eighteenth centuries.

*32. "*The Interaction of Sulphide with Sulphate and Oxide of Lead.*" By J. B. HANNAY.

In this paper the author examines the equations suggested by Percy to account for the smelting of lead in the reverberatory furnace. The two main reactions which are supposed to occur are usually represented by the equations $PbS+PbSO_4=2Pb+2SO_2$, and—

$$PbS+2PbO=3Pb+SO_2;$$

and although Percy relies on the first as representing what takes place, he also says that a mixture of the sulphate and oxide reduces the sulphide. The author finds that a much more complex reaction takes place, since metallic lead, when formed, attacks the remaining sulphate, producing litharge, which in its turn reacts with the sulphide, while some of the sulphide is removed by being dissolved in the metallic lead, and some is volatilised as the volatile compound PbS_2O_2. The result varies according to temperature and the method of mixing the substances. The following equations correspond with the results the author has obtained :—

(1) Lead sulphide and sulphate mixed in molecular proportions and very finely ground, and brought to calm fusion :—

$$12PbS+12PbSO_4=\underbrace{11Pb+2PbS}_{\text{Hard lead.}}+\underbrace{6PbO+2PbS+2PbSO_4}_{\text{Slag.}}+\underbrace{PbS_2O_2+16SO_2}_{\text{Fume.}}$$

34·8 per cent of lead was obtained instead of 76·3 as required by Percy's equation. When the sulphide of lead is in small pieces, the reaction yields more lead, but otherwise pursues a similar course :—

$$(2)\ 12PbS+12PbSO_4=\underbrace{14Pb+2PbS}+\underbrace{+4PbO+2PbSO_4+PbS}+\underbrace{PbS_2O_2+17SO_2}.$$

With excess of sulphate the result is :—

$$(3)\ 15PbS+12PbSO_4=\underbrace{15Pb+3PbS}+\underbrace{4PbO+2(PbS\cdot PbO)}+\underbrace{PbS_2O_2+20SO_2}.$$

On fusing lead sulphide and adding solid sulphate, the result is :—

$$(4)\ 3PbS+3PbSO_4=3Pb+2PbO+\underbrace{PbS_2O_2+4SO_2}.$$

On fusing the sulphate and adding solid sulphide, the result is :—

$$(5)\ 15PbSO_4+5PbS=12PbO+4PbSO_4+\underbrace{4PbS_2O_2+8SO_2}.$$

The temperature in this last case was much higher owing to the high melting-point of the lead sulphate, and thus a larger amount of fume was produced.

On mixing sulphate and oxide in the proportions which ought to form lead and sulphur dioxide, as by the equation :—

$$12PbS+6PbSO_4+12PbO=30Pb+18SO_2,$$

no such result was obtained, but the reduction took this form :—

$$12PbS+6PbSO_4+12PbO=\underbrace{16Pb+PbS}+\underbrace{+4PbO+4(PbS\cdot PbO)+PbSO_4}+12SO_2.$$

The author has shown in another paper, that the sulphide and oxide do not react to form lead, but combine together to form the substance PbS·PbO, which is the basis of lead slags.

DISCUSSION.

Professor ROBERTS-AUSTEN said that it would be within the recollection of the Fellows of the Society, that when Mr. Hannay's paper was read, on the 17th of May last, he pointed out that Mr. Hannay would be doing good service if he really added to our knowledge of the condensible products formed during lead smelting. Professor Austen, however, considered that the author's views had been stated in such a way as to fully justify chemists in asking for further evidence. The next morning Professor Austen had begun certain experiments on the lines indicated by Mr. Hannay. The President, also, appeared to have attacked the question, with the advantage of the co-

operation of Mr. Hannay. Mr. Hannay's statements presented themselves under two main aspects. It might be well either (1) to test the accuracy of his views as to the action of atmospheric air on sulphide of lead, or (2) to endeavour to obtain evidence as to the existence of volatile gaseous compounds of sulphide of lead. The speaker had adopted the latter course. He stated that he had understood Mr. Hannay to say distinctly, that if a mixture of sulphide and sulphate of lead were heated strongly no reaction ensued; hence Professor Austen's appeal in favour of the accuracy of certain of the equations which were given by Percy and accepted by metallurgists. He was glad, however, to find that Mr. Hannay did not maintain this extreme view. Professor Austen had experimentally confirmed the fact that the following equation is substantially correct:—

$$PbS+3PbSO_4=4PbO+4SO_2.$$

This is a very important point, as it is one of Percy's main equations; but he had pointed out on the previous occasion, that both this equation and the one which has hitherto represented the reaction between oxide and sulphide of lead are strongly endothermic, and in the case of an endothermic equation some explanation had to be sought; energy in some form had to be imported into the system, and an endothermic equation would represent a reaction which would be less likely to take place at a low than at a high temperature. In the case of the well-known endothermic interaction between carbon and the oxides of iron, it was probable that the iron carbonyl played an important part, which certainly pointed to the possibility of similar action on the part of *gaseous metallic* compounds in the metallurgy of lead. It had, therefore, appeared to him the conditions should be carefully studied; and he proceeded to state the results of the experiments he had instituted. First as regards the volatility of lead sulphide in various gases. The well-known statement, "that the volatilisation of sulphide of lead is promoted by currents of gas, such as proceed from the combustion of fuel," a statement made by Dr. Percy in 1870, might well be taken as a starting point. There could be no doubt that when galena is strongly heated in a porcelain tube between two plugs of asbestos in a current of sulphur dioxide, the galena is volatilised, and is driven right through the plugs, condensing on the other side of them. Such experiments were made in the School of Mines laboratory, the temperature being carefully measured by the aid of a thermo-couple, and it was found that at a temperature of 1357° C., 9 grms. of galena lost 38·2 per cent of its weight in sulphur dioxide in 20'; while 9 grms. of galena lost 37·7 per cent in nitrogen in 20'. At a still higher temperature, 1434° C., 9 grms. of galena lost 50·2 per cent of its weight in sulphur dioxide in 20'; while 9 grms. of galena lost 72·3 per cent of its weight in nitrogen in 20'. This result showing the volatility of galena in ordinarily pure nitrogen was not a little surprising; but Mr. Rose had made a perfectly independent experiment, the result of which confirmed the volatility of galena in nitrogen. Professor Austen had also ascertained the fact that at 1200° galena may be rapidly distilled *in vacuo*, and, so far, he had been unable to obtain any evidence in favour of the view that sulphur dioxide promotes the volatilisation of lead sulphide more than nitrogen does. He had, however, tried a further experiment. A kind of air thermometer was arranged, with a porcelain tube for a bulb, in which a certain amount of galena was placed in an atmosphere of sulphur dioxide. The tube was then heated strongly, and the expansion of the gas carefully measured by means of a moving index of mercury in a horizontal capillary tube. The presence of galena produced no abnormal change in the volume of sulphur dioxide such as might be expected to occur if a gaseous compound of sulphur dioxide and galena were formed. It should be remarked, however, that sulphur dioxide alone appears to exhibit contraction about 1000°, and the cause of this fact is being examined; but the presence of galena did not increase the observed condensation. Metallurgists would welcome the proof of the existence of gaseous compounds of lead sulphide; but although Mr. Hannay had undoubtedly shown that the whole metallurgy of lead should be further investigated, the existence, composition, and nature of the volatile compounds could not, as yet, be considered to be established.

Mr. Rose exhibited a porcelain tube in which 6 grms. of galena, contained in a boat between asbestos plugs, had been heated at 1300° for half an hour in a slow current of nitrogen, the temperature being taken by Le Chatelier's optical pyrometer. Practically the whole of the galena had been volatilised, and, passing through the plugs in both directions, had been condensed as crystals in the cold parts of the tube. He had tried to isolate the supposed compound, PbS_2O_2, by means of Deville's hot and cold tubes, galena being heated to about 1250° in a stream of sulphur dioxide, but had been unsuccessful, the sublimate on the cold tube consisting entirely of lead sulphide. It was to be remembered that several substances, such as ozone and oxide of silver, which, although more or less unstable a moderate temperatures, could exist at a white heat, had been compared in this way, and the method had appeared to be the most likely one to succeed in effecting the isolation of PbS_2O_2. The failure was therefore not without significance.

Mr. H. C. Jenkins said that some experiments had been carried out in the metallurgical laboratories of the Royal College of Science. It was found that lead sulphide (galena) was easily volatile in a vacuum at a temperature only a few degrees above its melting-point. In a current of sulphur dioxide the rate of volatilisation was, as would be expected, much increased, but a similar current of nitrogen gave even better results than sulphur dioxide. Very careful experiments were made with mixtures of galena and sulphate of lead, but, although some of the products resembled those that Mr. Hannay had described, yet the evidence obtained did not point to the existence of a volatile compound PbS,SO_2. In some cases only the acting compounds were present; in others, the experiments were performed in an atmosphere of sulphur dioxide in the presence of furnace gas. Metallic lead was only seen as a separate product in the latter case. But it was found that pure metallic lead is capable of decomposing sulphur dioxide, forming sulphur and oxide. Experiments were still in progress with a view to obtain quantitative knowledge of the change. The existence of volatile lead compounds would, if proved, offer an easy explanation of the cause of lead fume, but in view of the volatile character of well-known compounds of lead at furnace temperatures, much more experimental evidence than has yet been afforded is needed to demonstrate the formation of new compounds.

The President said that the discussions to which Mr. Hannay's papers had given rise were of considerable value in calling attention to the many interesting points in the metallurgy of lead which still required investigation. The main question around which the interest of the discussion centred was that relating to the existence of volatile compounds of lead sulphide. The experiments which he had witnessed certainly favoured the conclusion that sulphur dioxide exercised a specific effect in volatilising lead sulphide; but assuming that the evidence that combination took place was satisfactory, he could not regard Mr. Hannay's observations on the extent to which volatilisation took place as satisfactory determinations of the composition of the volatile compound; such a compound would probably be dissociable, and, if so, it was not to be expected that the gas and galena would pass over and be collected in exact molecular ratios. The strongest evidence was undoubtedly that derived from passing air into molten galena; the manner in which galena volatilised and passed away as lead sulphate under such conditions was extraordinary, and still more remarkable was the fact that, as Mr. Hannay stated, just half the lead was obtained in the metallic state. Experiments made

in his laboratory, under Mr. Hannay's direction, had given this result, and it was certainly a remarkable coincidence if the result were but accidental. It appeared to him that, although Mr. Hannay could not be held to have established his point, he had called attention to peculiarities in the behaviour of lead sulphide which were of great interest to metallurgists, and that he had clearly made out a case for enquiry.

Mr. HANNAY, in reply, said that he was glad to find it was now recognised that the simple equations of the text-books did not adequately represent the facts, and that nearly all the furnace reactions of lead compounds were very complex. As to the volatility of the sulphide and the formation of a definite compound with sulphur dioxide, this conclusion was based on the action of air on molten galena, an action which always proceeded in the same manner, and was represented by the equation—

$$2PbS + O_2 = Pb + PbS{\cdot}SO_4,$$

as exactly one-half of the galena is reduced to lead and left in the metallic state, and one-half is volatilised with the sulphur dioxide. Whether this was a definite compound or a mere chance volatility in molecular proportions was a question which might still admit of experimental investigation, and it was to be hoped that some of those who had spoken would carry the work further. As showing that sulphur dioxide when set free in intimate contact with molten galena, does act in a special manner, it might be stated that while nitrogen and hydrogen gases passed at the rate of 1 litre in three minutes through the molten sulphide, carried over the galena as vapour at the rate of 3·5 grms. per litre of gas passed, air under the same conditions carried over 5·2 grms. per litre. Now if the amount carried over by the nitrogen of the air were the same as that carried over by pure nitrogen, there is a large excess carried over by the sulphur dioxide (formed by the combination of the oxygen of the air with the sulphur of the galena), and this excess is present in nearly the proportion indicated by the formula $PbS{\cdot}SO_2$ or PbS_2O_2. All the evidence pointed to the fact that when sulphur dioxide was formed in intimate contact with molten galena, every molecule of sulphur dioxide rendered volatile 1 molecule of galena, and subsequently deposited it on cooling. The volatility is so profoundly modified by temperature, that experiments are not comparable unless carried out at the same temperature, a result difficult to obtain, but Mr. Hannay hoped that Professor Roberts-Austen would test the matter, and lay down accurate data for future work, as all statements of temperature had hitherto been only the roughest of approximations.

*33. "*The Mineral Waters of Cheltenham.*" By T. E. THORPE, D.Sc., F.R.S.

This communication contains the result of the analysis of the waters of the following wells:—(A.) (1) Well Place; (2) Christchurch Road. (B.) (1) Lansdowne Well; (2, 3, and 4) Pitville Spas. The determinations, so far as applicable, are compared with the results of analyses by Abel and Rowney, made in 1847, from which it appears that the waters have experienced no sensible alteration in composition during the last half century.

*34. "*The Oxidation of Tartaric Acid in presence of Iron.*" By H. J. H. FENTON, M.A.

This paper gives an account of the investigation undertaken by the author to explain the cause of a peculiar colour reaction of tartaric acid observed by him some years ago. Free tartaric acid, or a soluble tartrate, is oxidised by certain agents in presence of a trace of ferrous salt, when, on addition of alkali, a beautiful violet colour is produced.

The isolation of the substance which gives rise to this colour was, in the first instance, a matter of considerable difficulty, owing to the unstable nature of the solution, but a method has now been devised whereby it can be obtained in considerable quantities and in a state of purity. It has the appearance of a shining, white, crystalline mass with a pearly lustre. The crystals are quite permanent in the air, but effloresce over sulphuric acid or when heated. Analyses and molecular weight determinations by different methods show that the substance is a dibasic acid of the formula $C_4H_4O_6$, which crystallises with $2H_2O$. It is very sparingly soluble in cold water, acts as powerful reducing agent, and gives a violet colour with ferric chloride in presence of alkali, changed to a transient green by acids. On heating with hydrogen iodide, it gives succinic acid, glycotartaric acid being an intermediate product. The aqueous solution decomposes slowly at ordinary temperatures, and rapidly on heating, giving carbon dioxide and an aldehydic substance which is under examination. Phenyl hydrazine gives two crystalline compounds, one a brilliant silver-white, and the other golden-yellow.

The methyl salt is volatile at about 150°, and may be sublimed in crystals; the ammonium, sodium, and barium salts also are easily obtained in the crystalline form. The acid somewhat resembles dioxytartaric acid in the sparing solubility of its sodium salt, but differs considerably from that acid in other respects.

The constitution of the acid will be considered in a future communication, but the author intends also to investigate several side issues suggested by this work, suce as the detection of peroxide of hydrogen under certain conditions, the preparation of glyoxylic acid, and the oxidation of other substances in presence of ferrous salts.

*35. "*The supposed Relation between the Solubility of a Gas and the Viscosity of its Solvent.*" By T. E. THORPE, F.R.S., and T. W. RODGER.

In the *Zeit. für Physik. Chem.*, ix., 171, 1892, appeared a short communication by L. W. Winkler, in which he attempted to account for the fact that the solubility of a gas in water diminished with rise in temperature. The conclusions which he arrived at may thus be stated:—

(1) For the same gas the percentage diminution in its absorption coefficient for any temperature-interval is proportional to the corresponding percentage diminution in the viscosity of the solvent.

(2) For any gas the percentage diminution in its absorption coefficient for the same temperature-interval is proportional to the cube root of its molecular weight.

These conclusions were based on Winkler's own observations on the absorption coefficients of hydrogen, oxygen, nitrogen, nitric oxide, and carbonic oxide in water, and on the relative numbers given by Graetz for the viscosity coefficients. The authors, when endeavouring to ascertain how far these deductions were affected on employing the values recently obtained by them for the viscosity coefficients of water, have found that owing to imperfect mathematical treatment, Winkler's conclusions have to be modified. The deductions which the facts appear to warrant are:—

(1) For the same gas the diminution in solubility, and not the percentage diminution, is proportional to the corresponding diminution in viscosity.

(2) For any gas, the factor of proportionality is greater the greater its molecular weight, although the two do not appear to be simply related to one another.

The authors also call attention to the fact that since the viscosities of a large number of organic liquids at different temperatures have now been determined, lack of data concerning the solubility of gases in such solvents alone stands in the way of a more complete investigation of the interdependence of solubility and viscosity.

*36. "*The Specific Character of the Fermentative Functions of Yeast Cells.*" By ADRIAN J. BROWN.

The usually accepted view as to the cause of the exhi-

bition of the fermentation functions of yeast cells is, that it is a starvation phenomenon brought about by want of free oxygen during the life of the cells in a fermentable liquid: or, more briefly, that it is a phenomenon of "life without air." This view was originated by Pasteur, a full account of the experimental results which led him to formulate this theory being given in Chapter VI. of his "Etudes de la Bière."

In a paper on the influence of oxygen on alcoholic fermentation (*Journ. Chem. Soc.*, lxi., 369), attention was called by the author to the fact that some of the experimental results described appeared to be contradictory to Pasteur's theory. Further work on this subject has led him to think that a review of the experiments on which Pasteur's theory rests, in conjunction with the results of some of his own, will not be out of place at the present time.

Pasteur's experiments may be divided into two classes, one containing experiments which appear to have suggested his theory, the other containing experiments undertaken for the purpose of proving its truth. It is not proposed to discuss the experiments in the first class, as, although they demonstrate most important facts regarding the life and growth of yeast, they afford no proof that fermentation is a consequence of "life without air."

The attempted proof of this theory lies in those experiments by which Pasteur determines, under varying conditions of aëration, the proportion of the weight of the yeast formed to the weight of sugar fermented. This ratio, or proportion, of yeast to sugar is, Pasteur considers, an expression of fermentative power; and when considering the ratios established by different experiments, he treats them as comparable with each other. By thus comparing fermentative powers of yeast cells under varying conditions of aëration, he arrives at the conclusion that when aëration is perfect, fermentative power ceases, and when aëration is reduced, fermentative power increases: the *proof* of Pasteur's theory, indeed, rests upon this conclusion.

As so much turns on Pasteur's interpretation of the experimental results by which he determines fermentative power, it is desirable to test it as thoroughly as possible. The ratio of yeast formed to sugar fermented in any experiment is an expression of fermentative power; but if it is found desirable to *compare* fermentative powers determined from the results of two or more experiments, it becomes necessary to make sure that either the total fermentative power, or some known fraction of it, has been measured in each case, otherwise no true comparison can be made.

The ratios determined in Pasteur's experiments are used as though they represented the total fermentative powers of the yeasts concerned; but there is no evidence in support of this, and they may represent unknown fractions of the powers equally as well. In the majority of Pasteur's experiments the sugar used was completely fermented, and exhibition of fermentative power by the yeast was thus limited by the amount of the sugar originally present in the fermentable liquid; but there is no evidence that, under these conditions, the yeast had exerted all its fermentative power. If the amount of yeast formed during fermentation were in direct proportion to the sugar fermented, the ratio of yeast to sugar would remain constant, however much or little sugar were available; but experiments made by the author show conclusively that such is not the case. The amount of sugar available during fermentation is a factor that has but little influence on yeast increase; *there is, in fact, no direct proportion between weight of yeast formed and sugar fermented.* In order to show that the total fermentative power of yeast has not been measured in Pasteur's experiments, a fermentation was carried on under aërobic conditions until the sugar originally present was decomposed. Afterwards, using the principle of overcrowding as a means of preventing reproduction, the crowded cells were fed with more sugar. Feeding was carried on at intervals until the yeast had fermented three times the amount of sugar originally present at the beginning of the experiment, but no increase in the weight of yeast took place. Thus the fermentative power of the yeast was found to be at least threefold what it would have been if determined in the manner adopted by Pasteur. In most of Pasteur's experiments under aërobic conditions, the apparent deficiency in fermentative power of the yeast was doubtless due to the quantity of sugar on which the yeast could exert its power being limited in amount.

In two experiments Pasteur estimated fermentative power under aërobic conditions, the yeast being in contact with sugar at the termination of the experiment, viz., in his experiments carried on in shallow dishes in order to expose the yeast to the maximum aëration possible. Pasteur believed that, under these conditions, the fermentative power of yeast was reduced to such a point that practically the yeast was no longer a ferment, but lived the ordinary life of a fungoid growth in air. But these experiments are open to the serious objection that, as they were allowed to continue during but a limited time, a *time* factor is introduced. Pasteur himself maintains that *time* had nothing to do with fermentative power, yet it enters into the question when considering these experiments. Moreover, as cane-sugar was used in these experiments, it must have been inverted before being fermentable. The author finds that inversion proceeds very slowly under the conditions of Pasteur's experiments. As inversion must precede fermentation, and is a function of the yeast cell apart from that of fermentation (J. O'Sullivan, *Trans.*, lxi., 593), Pasteur's measure of fermentative power in the experiments referred to is an expression of the action of the inversion and fermentation functions of yeast cells in a limited *time*. Under these circumstances no reliance can be placed in the figures Pasteur gives as representing the true fermentative power of the yeast.

Apart from the fact that Pasteur fails to prove the truth of his theory by comparing fermentative powers, his hypothesis is further weakened by the fact that none of the results of his experiments are contradictory to a hypothesis opposed to his. The aërobic and anaërobic life-history of yeast, as demonstrated by Pasteur, can be accepted without the truth of his hypothesis regarding fermentation being admitted. There is no *primâ facie* reason why the fermentation functions of yeast cells should not be exercised independently of the cells environment, so far as the presence or absence of free oxygen is concerned; and nothing in Pasteur's experiments contradicts this.

37. *Observations on the Influence of Temperature on the Optical Activity of Organic Liquids.*" By Percy Frankland, Ph.D., F.R.S., and John MacGregor, M.A.

The authors, after referring to the few isolated observations by Pictet, Perkin, and others, give the results of the polarimetric measurements which they have made at different temperatures between 0° and 35° C. with some of the ethereal salts of active glyceric and diacetylglyceric acids. Owing to the comparatively unstable nature of the ethereal salts of glyceric acid, caution has to be exercised, or the effect of decomposition may be mistaken for the influence of temperature. It is shown that these glycerates have a tendency, especially at higher temperatures, to partially decompose into alcohol and glyceric anhydride, and the latter remaining in solution in the undecomposed ethereal salt and alcohol, causes an increase in lævorotation. By avoiding this source of error, however, it is shown that the rotation of methylic and ethylic glycerates undergoes very marked increase as the temperature rises, the increase being greater in the case of the methylic than in that of the ethylic compound. The influence of temperature on the rotation of the diacetylglycerates is considerably greater, and, owing to their stability even at high temperatures, they lend themselves better to observations of this kind than do the glycerates. The results obtained with the glycerates and diacetylglycerates have been summarised, whilst for comparison there are also

recorded the corresponding figures calculated from Pictet's determinations made with the tartrates at 20° and 100° C.

In each of the three series of homologous compounds the percentage increase in rotation for a given rise in temperature is greatest for the methyl, and then for the ethyl, compound, whilst the higher members of each series exhibit in general successively smaller increments. Reference to the previous paper will show that it is precisely in the first few members of each series also that the addition of CH_2 causes the greatest increase in rotation, or, in other words, in those cases in which the degree of molecular dissymmetry is most increased by a rise of temperature, the dissymmetry is also most increased by an addition of CH_2, and *vice versâ*.

38. "*The Maximum Molecular Deviation in the series of the Ethereal Salts of Active Diacetylglyceric Acid.*" By Percy Frankland, Ph.D., F.R.S., and John MacGregor, M.A.

The authors have previously shown that in the homologous series of the ethereal salts of active glyceric acid, the rotation is increased by each addition of CH_2 in passing from methylic glycerate to normal butylic glycerate, whilst higher in the series the further addition of CH_2, on the contrary, leads to a diminution in the rotatory power. This culmination of the rotatory power in the butylic glycerate is most strikingly exhibited by calculating what has been termed by Guye the *molecular deviation*, $[\delta]_D$, for each of the members of the series, according to the formula—

$$[\delta]_D = \frac{a}{L}\sqrt[3]{\frac{M}{d}},$$

in which a is the observed angle of rotation, L the length of the polarimeter tube, M the molecular weight, and d the density.

The authors show in the present paper that there is the same phenomenon of a maximum rotation in the series of the ethereal salts of diacetylglyceric acid, and that this maximum is again reached at much the same point in the series, for whilst the rotation rises successively in passing from methylic to isobutylic diacetylglycerate, the normal heptylic and octylic compounds already exhibit a falling off in the rotation. The curves representing the molecular deviation of the ethereal salts of glyceric and diacetylglyceric acids respectively are in fact found to be roughly parallel, each diacetylglycerate possessing a rotatory power which is in excess of the rotatory power of the corresponding glycerate by a difference which does not undergo much change throughout the series.

A particularly interesting feature in the series of diacetylglycerates is the circumstance that in the methyl compound there are two groups of equal mass, and again, in the ethyl compound, two other groups of equal mass attached to the asymmetric carbon atom, but these relations are not attended with any change of sign throughout the series.

The authors have also commenced studying the effect of replacing the hydroxylic hydrogen in glyceric acid by higher negative radicles than acetyl, and have found that whilst methylic dipropionyl glycerate is slightly inferior in lævorotatory power to methylic diacetylglycerate, methylic dibenzoylglycerate is powerfully dextrorotatory.

(To be continued.)

The Essence of Ylang-Ylang.—A. Reychler.—The essential oil of ylang-ylang, in which previously only benzoic and acetic acids had been recognised, contains numerous substances. Benzoic and acetic acids (etherified) figure there in the respective proportions of 9 and 7 per cent. Ylangol forms from 30 to 32 hundredths of the oil, and sesqui-terpene forms also a considerable proportion.—*Bull. de la Soc. Chim. de Paris*, xi.-xii., No. 12.

NOTICES OF BOOKS.

Organic Chemistry. Part I. By W. H. Perkin, jun., Ph.D., F.R.S., Professor of Organic Chemistry in the Owens College, and F. Stanley Kipping, Ph.D., D.Sc., Lecturer and Assistant in the Chemical Research Laboratory, Central Technical College, City and Guilds of London Institute. London and Edinburgh: W. and R. Chambers, Limited, 1894. Small 8vo, pp. 302.

This work was originally intended to be based on the syllabus of the Science and Art Department, but its scope was enlarged so as to be more useful to general students.

The present part is concerned with the fatty compounds. It includes a general and ably written description of the methods followed in the separation, purification, and analysis of the organic compounds, and in the determination of molecular weights.

Constitutional questions are discussed at an early stage, and the facts are brought forward on which the given constitutional formulæ are based.

Those parts of the text which are of less importance, or which are suitable for the advanced student only, are printed in smaller type.

The authors most rightly insist on a thorough course of practical work to be performed by the student himself. The work is eminently calculated to prove useful to students of organic chemistry.

Milk-testing and Payment for Milk by Results. By C. C. Lance, Secretary Euroa Butter Factory. Melbourne: Tytherleigh and Bayne, 367*a*, Post Office Place West. Second Edition.

It may seem strange that the very words which, if used with reference to national education, savour of epidemic lunacy should, if applied concerning the dairy industry, herald the dawn of common sense.

The author very rightly insists that milk, like other commodities which vary in value, should be sold not by quantity alone, but by quality. The quality is judged by the proportion of fatty matter—butter—in each sample. This capital point he ascertains, not by means of the lactometer, which he rightly regards as utterly delusive, but by the "Babcock tester." Speaking on behalf of the dairy factory, whether it mainly produces butter or concentrated milk, he insists upon daily sampling. For this purpose he has devised an appliance by means of which the milk supplied to a factory by, say, twenty farmers can be sampled automatically with perfect fairness and accuracy. The daily samples thus taken on behalf of each farmer are kept in separate bottles to the end of the week, when they are tested.

To prevent the samples spoiling in the interim, each receives a small addition of a sterilising substance. Among such the author prefers "formaline," a proprietary nostrum, which *may* be harmless. But as these samples are merely kept for testing and not for sale, the properties of the preservative are of no special importance.

Each sample is tested at the expiry of the week in the Babcock apparatus here figured, and the value of each is determined according to its proportion of butter-fat.

The system appears to have been generally adopted in the Victorian dairy factories,—perhaps, we might say, in those of Australia at large,—and gives general satisfaction.

The only question seems to be whether the Babcock tester and the Lance system can be adopted to the retail milk trade? Every consumer of milk in modern cities, whether in the Colonies or at home, or in alien lands, must know that he rarely meets with milk as delivered by the cow.

If the system described in the pamphlet before us can touch fatally the frauds of the trade, the author will deserve to rank not merely as a Colonial, but as an Imperial, or even an international, benefactor.

Repetitorium der Chemie: Mit besonderer Berücksichtigung der für die Medizin wichtigen Verbindungen sowie des "Arzneibuches für das Deutsche Reich" und anderer Pharmakopäen, namentlich zum Gebrauche für Mediziner und Pharmazeuten. (Repetition Book of Chemistry; Drawn up with especial reference to Compounds important in Medicine and to the "Arzneibuch" of the German Empire, as well as to other Pharmacopœias, especially for the use of Physicians and Pharmaceutists). By Dr. CARL ARNOLD, Professor of Chemistry at the Royal Veterinary High School at Hanover. Sixth Improved and Enlarged Edition. Small 8vo, pp. 613.

THIS work has evidently given great satisfaction, since in ten years it has passed through six editions. It is evidently adapted more especially to the requirements of medical men and pharmaceutists. As intimated in the prefaces, it serves as key or guide book to the courses of lectures as well as a work of reference, to which end it is provided with a very comprehensive index. Chapters have been introduced on thermochemistry, on dissociation, and on stereochemistry, and the chapters on the determination of molecular weights and the examination of chemical structure have been remodelled.

The question of nomenclature is considered at some length. The attempt is made to explain the Latin names used in Germany by physicians and pharmacists, which seem as if designed for the very purpose of confusion. Surely the first duty of an international congress on chemical nomenclature should have been the condemnation of this medical Latin, which obtrudes itself even into price lists.

In speaking of the classification of the elements, we perceive that the unhappy term metalloids is still retained.

We observe with great satisfaction that the author regards it as probable that the elements have been elaborated from one primitive substance or from a few such substances.

We find bismuth, germanium, tin, and lead placed among the non-metals.

As the only trustworthy reaction for ozone, the author cites the deep violet colouration which it produces on paper which has been steeped in tetramethylparaphenylendiamine.

On a thorough perusal of the work before us, we must bear witness to its comprehensiveness, accuracy, and admirable arrangement. To all who understand the German language it must be recommended as an excellent text-book.

Chemistry and Physics: A Manual for Students and Practitioners. By JOSEPH STRUTHERS, D. W. WARD, and CHARLES H. WILLMARTH. The Students' Quiz Series, edited by BERN B. GALLAUDET. Philadelphia: Lea Brothers and Co., *n.d.*, 1893. Pp. vii. and from 17 to 288, 12mo. Illustrated.

As the authors themselves inform us, the object of this manual is to collect sufficient material on the sciences of chemistry and physics to cover the subjects as taught in a general collegiate or medical course. It is not intended to displace either text-book or lectures, but to be used as an aid by students entering upon the threshold of the sciences, as an auxiliary to lectures, and by teachers in review work. The three authors seem to have worked at different sections of the book—Mr. Struthers on inorganic chemistry, Mr. Ward on the organic, and Mr. Willmarth on physics. The two former are connected with the Columbia College School of Mines, New York City.

This work forms one of a series prepared under the supervision of Dr. B. B. Gallaudet, of New York, for the special use of medical students, the twelve other volumes dealing with anatomy, surgery, practice of medicine, and special diseases. The book is arranged on the catechism plan, and much as we object to this form of instruction, we admit that it shows very careful preparation, and covers the field of elementary chemistry quite fully.

Since no book-review is now written without adverse criticism, we must find some fault with the work in hand, so we merely say that less attention is paid to the medical and toxicological side of chemistry than would be expected of a work written for medical students. For example, under Arsenic Marsh's test is the only one mentioned, and under Iron the blast-furnace process and the uses of crucible steel are quite fully treated, whereas the physiological and medical qualities of iron are casually mentioned in two lines. Again, in the section of organic chemistry the medical student will find twenty-two pages on the aromatic series, and only nine lines on the albumens. At the same time the student who will master the contents of this little volume will be able to reply to any examination questions likely to be put to him by the most exacting teacher.

As the work is designed for use in American colleges, the authors and editor would have done well to adopt the rules for spelling chemical terms adopted by the American Association for the Advancement of Science and promulgated through the Bureau of Education. The typographical appearance of the volume is excellent; the illustrations with one exception are confined to the section of physics.—H. C. B.

CORRESPONDENCE.

NOTE ON THE MARSH TEST.

To the Editor of the Chemical News.

SIR,—An instance recently came under my observation illustrating the necessity for careful removal of organic material before applying the Marsh test in toxicological work.

A portion of the fluid contents of a stomach was given a chemist at the time of the autopsy, and he forthwith poured the same into a Marsh apparatus, with negative result.

From the balance of the material I afterwards separated a fatal dose of arsenic, but the defence naturally made the most of the conflicting evidence. To illustrate the interference of organic matter, it was shown that negative results followed with certainty if the quantity of organic matter were large, and that albumenoid material, such as blood, was especially liable to arrest all action.—I am, &c.,

WM. P. MASON.

Rensselaer Polytechnic Institute, Troy, N.Y.,
July 6, 1894.

Errors in the Detection of Sugar in Urine.—Dr. Sir George Johnson, in conjunction with his son Mr. G. Stillingfleet Johnson, Demonstrator of Chemistry at King's College, finds that the reduction of copper, generally ascribed to glucose, is in many cases due to kreatinine. Hence the examination of urine for sugar is preferably effected by means of picric acid, as described by Sir G. Johnson in the *Lancet*. If to a drachm of normal urine, in a test-tube of about $\frac{1}{2}$ an inch in diameter, there is added an equal volume of a saturated solution of picric acid and $\frac{1}{4}$ drachm of liquor potassæ, the mixture at once becomes red. If glucose is present, the liquid, on being treated as above described, gives so dark a colour that no red light is seen through the middle of the column of liquid. (See Mr. G. Stillingfleet Johnson's paper in the *Proceedings of the Royal Society*, vol. xliii., p. 453.)

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxix., No. 1, July 2, 1894.

Researches on Phenylhydrazine. Action of Oxygen and of Water; Formation of Salts.—M. Berthelot.—The author's recent experiments verify afresh a law which he has established by a multitude of thermic experiments upon dissolved salts; that is, the strong acid combines with the strong base, forming entirely or approximately the salt which is most stable in presence of water, which is at the same time that whose formation in the solid state evolves most heat. In consequence of the constitution of this salt in the midst of the liquid the weak acid remains in presence of the weak base, so as to form the most dissociated salt. From this increase of dissociation there results a considerable absorption of heat, the numerical value of which demonstrates the existence of a reaction almost complete. These phenomena are in contradiction with the announcement of a saline thermo-neutrality; they are thus in contradiction with the real ideas of Berthollet, such as he has formulated them in the most explicit manner.

Impurities of Industrial Aluminium.—Henri Moissan.—Industrial aluminium contains, besides iron and silicon, a small quantity of carbon and traces of nitrogen. These substances decidedly modify the properties of aluminium.

Preparation of a Crystalline Aluminium Carbide.—Henri Moissan.—This paper will be inserted at some length.

"Chemistry in the Living Cell."—Armand Gautier. This paper accompanied the presentation of a work which the author has just published under the above title. He shows that all or nearly all the cells of the animal economy are at once the seat of a double function, aërobic and anaërobic. In the depth of the albumenoid protoplasm of the cell there are produced in a continuous and regular manner phenomena of hydration and even of reduction, with exclusion of all intervention of foreign oxygen. In the peripheric parts of the cell the products which have been formed in the absence of oxygen are then submitted to the action of this gas and are ultimately burned.

Application of the Cathodic Rays to the Study of Variable Magnetic Fields.—Albert Hess.—The author remarks that the cathodic rays have recently been made the subject of a very extensive study by P. Lenard, who completes the work published on this subject by Hittorf, Crookes, Goldstein, Hertz, and other physicists. From his own point of view, *i.e.*, the utilisation of some of the properties of these rays for the study of magnetic fields, he retains only the following results of these researches:—1. The cathodic rays can traverse slender sheets of metal. 2. These rays, although they can be *produced* only in very rarefied media, can be propagated in all gases at all pressures, but the sheaf is so much less diffused as the pressure of the gas is more feeble. 3. The magnet deflects the cathodic rays; the deflection, which varies with the intensity of the field, is not due to a direct action of the magnet upon the rays themselves, but to a magnetic deformation of the medium, that is of the ether. 4. With equal conditions of production and with the same intensity of the field the deflection of the sheaf is the same for all gases and at all pressures. 5. The cathodic rays act upon the photographic film.

Researches on the Action exerted by the Acid Sodium and Ammonium Molybdates upon the Rotatory Power of Rhamnose.—D. Gernez.—Slight additions of molybdates occasion a relatively great increase of rotation. One-twelfth of the molecular weight is sufficient to raise the rotation from 1·14° to 2·11°. 2. The addition of $\frac{6{\cdot}75}{24}$ of the molecular weight gives rise to a maximum effect which corresponds to the rotatory powers $[\alpha]_D$ 18 = 22·95° for acid sodium molybdate and 19·91° with acid ammonium molybdate. 3. Large quantities of these salts produce no appreciable change. 4. The maximum effect is here found realised for relative weights of the molybdates equal to those which give the same effects in the case of mannite, sorbite, and perseite.

Change of Sign of the Rotatory Power.—Albert Colson.—The author shows that there exist compounds possessing a rotatory power varying with the temperature to such a degree as to change the sign, as in the case of isobutyl amylic oxide. In certain cases these great variations are occasioned by chemical equilibria.

The Line-Spectra of Sulphur and on its Recognition in Metallic Compounds.—A. Aymonnet.—The author, on continuing the study of the spark-spectra of the metallic sulphides, has observed certain groups of fine rays slightly detached from the green part of the spectrum the wave-lengths of which coincide with those of the principal lines of the so-called secondary spectrum of sulphur. This has been obtained hitherto by passing the condensed induction spark into a Plücker tube filled with vapour of sulphur at a low pressure. He has endeavoured to satisfy himself that we may obtain the same spectrum under ordinary conditions of temperature and pressure by causing the spark of the induction coil to strike between two platinum wires or between two rods of retort-coke covered with pure sulphur, melted and allowed to cool. On operating without a condenser the sulphur ignites and gives a spectrum continuous and slightly luminous. But if we interpose in the induced circuit a condenser of from 40 to 50 square decimetres, we obtain the beautiful line spectrum figured in the original. The group of the red and the green have a striated aspect by which they can be easily recognised. To take account of the principal rays of the air (Masson's, condensed spark), especially in the violet, where the intensity of the bands is of the same order, we have had recourse to the juxtaposition of the two spectra. The groups Sα, Sβ, Sγ are very bright with a strong condenser. The intensity of the rays is scarcely less than those of the metals. The group Sε, less strong, is seen well notwithstanding α (500) of the air, which it is difficult to get rid of. The groups Sδ, Sζ, Sη, Sθ are quite visible. Sμ is less distinct and Sπ and Sρ are very diffused. The vague band between 152 (469·5) and 161 (456) is not easily distinguished from the band ε of the air (465) to (460). Having satisfied myself of the existence and the position of the rays of sulphur in the condition in which I operated, I found them in the metallic sulphides already studied, with the experimental arrangement already described (Session March 12, 1894, p. 591), but increasing the surface of the condenser. The spectrum of the mineral and that of sulphur were placed in juxtaposition in the field of the spectroscope by means of a total reflection prism, the two sparks being taken in the same condensed induction circuit. We have thus found the perfect prolongation of the rays of sulphur from one spectrum to the other for all the sulphides, sulpho-antimonides, and sulpho-arsenides examined. The groups Sα, Sβ, Sγ, Sδ, Sε, Sζ, Sη, Sθ are the most characteristic of sulphur in these metallic compounds. It is advantageous to adapt to the eye-piece of the spectroscope sliding shutters enabling us to limit the field and isolate a small part of the spectrum. Nevertheless certain sparkling metallic rays extinguish by the irradiation the neighbouring sulphur groups. The author then describes the spectra of a number of sulphur minerals. By this method we recognise minute quantities of sulphur. The author has thus found in the spectrum of selenium, sold as pure, the groups of Sα and Sβ and the rays of arsenic.

New Researches on the Bromo-boracites.—G. Rousseau and H. Allaire.—The author describes the bromoboracites of magnesium, zinc, cadmium, manganese, cobalt, and nickel.

Influence of Pressure on the Combination of Hydrogen and Selenium.—H. Pélabon.—The author's results show that an augmentation of pressure increases very slightly the quantity of hydroselenic acid produced at a given temperature. This influence is most felt at the lowest temperature.

A Reaction of the Aldehyds. Differentiation of the Aldoses and Cetoses.—A. Villiers and M. Fayolle.—This paper will be inserted in full.

Substitutions of Alcoholic Radicles Linked to Carbon and to Nitrogen.—C. Matignon.—A reclamation of priority as against H.H. Stohmann and Langbein.

On Piceine, a Glucoside of the Leaves of Pinus picea.—M. Tanret.—Piceine, hydrated or anhydrous, crystallises in prismatic silky needles, soluble in 1 part of boiling water and in 50 parts at 15°, in 20 parts of alcohol at 70°, 68 parts at 90°, and 534 parts of absolute alcohol in the cold (15°), 33 parts of absolute boiling alcohol, and 123 parts of acetic acid at 15°. It is insoluble in ether and chloroform. Piceine is lævo-rotatory: $\alpha_D = -84°$ in solution in water and $\alpha_D = -78°$ in solution in alcohol at 70°. Anhydrous piceine melts at 194°. Under the action of emulsine piceine fixes a mol. of water and is split up into glucose, $C_6H_{12}O_6$, and piceol, $C_8H_8O_2$. Piceine is neither precipitated by tannin nor by basic lead acetate. Piceol behaves as a monatomic phenol.

Presence of Hydrogen and Hydrogen Monocarbide in the Residual Nitrogen of Blood.—D. de Saint-Martin.—1 litre of ox-blood yield at 0° and 760 pressure—

	I.	II.
Hydrogen..	0·41 c.c.	0·64 c.c.
Hydrogen monocarbide..	0·69 „	0·68 „

Action of Sulphuric Acid upon Camphene.—G. Bouchardat and J. Lafont.—The products of the reaction are the ether of the borneol of inactive camphene, the borneol sulphuric acid yielding on further saponification the borneol of inactive camphene, and lastly a small quantity of the polymers of camphene.

Bromo-derivatives of Perchloric Ethylene.—A. Besson.—Not adapted for useful abstraction.

Novel Organo-Metallic Compounds.—G. Perier.—The author describes the acetanilide-aluminium chloride, the butyranilide-aluminium chloride, and the compounds of butyranilide and of acetoparatoluidine with aluminium chloride.

Formation of Succinic Acid and of Glycerin in Alcoholic Fermentation.—J. Effront.—The chief quantities of glycerin and of succinic acid are formed when the fermentive power of the yeast is almost exhausted.

Influence of Chlorides upon Nitrification.—J. Crochette and J. Dumont.—Soils which have received potassium chloride in the proportion of 0·50 grm. per kilo. nitrify twice better than normal soil which has been freed by washing from calcium chloride. This explains why in rainy years chlorides are favourable, whilst in dry seasons this effect is null and positively hurtful.

MISCELLANEOUS.

The Institute of Chemistry of Great Britain and Ireland.—At the Examination in Practical Chemistry for admission to the Membership of this Institute, held at the Laboratories at 30, Bloomsbury Square, from July 2nd to 5th, 27 candidates presented themselves, of whom the following 17 were successful:—A. Adams (trained at Mason College, Birmingham), H. Bowes (Assistant to W. Thomson, F.I.C.), B. S. Bull (Christchurch University, New Zealand), O. F. C. Block (Finsbury Technical College and student under J. Hodgkin, F.I.C.), W. C. Carter (Finsbury Technical College), W. Crossley (Royal College of Science, Dublin). W. R. Hardwick and J. Harger (University College, Liverpool), J. A. Hatfield (Mason College, Birmingham), G. H. Perry (Royal College of Science, London), W. Ralston (Glasgow and West of Scotland Technical College), A. Ross and H. C. Seabrooke (Finsbury Technical College), T. C. Sharrott (Mason College, Birmingham, and Royal College of Science, London), E. A. Warmington (Mason College, Birmingham, and Leipzig University), and J. T. Whitton (Glasgow and West of Scotland Technical College). The Examiners were Professor Wyndham R. Dunstan, M.A., F.R.S., F.I.C., and Mr. Thomas Fairley, F.R.S.E., F.I.C. The Members of the Institute now number over 850, and there are over 200 Registered Students.

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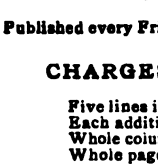

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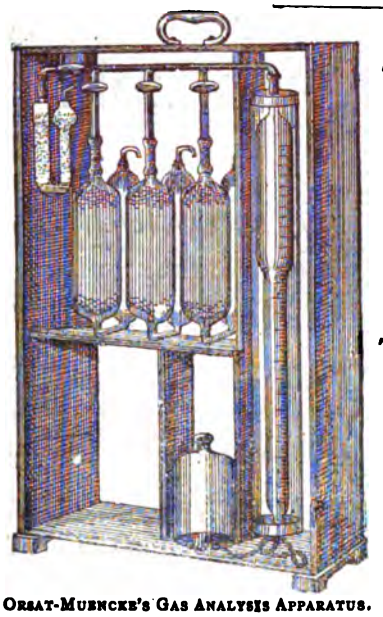

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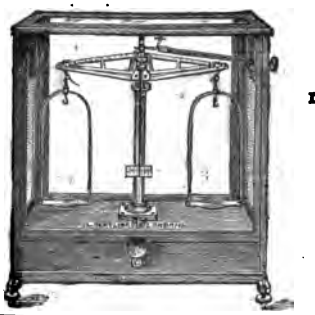

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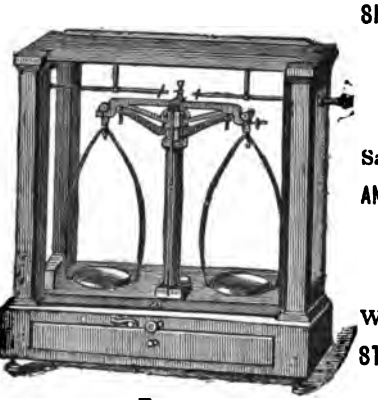

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HEATING-POWER OF SMOKE.

By R. R. TATLOCK, F.R.S.E., F.I.C., F.C.S.

It appears to be generally understood that a large percentage of fuel is lost in the smoke which issues so abundantly from most chimneys, and random statements have been made to the effect that the loss in heating-power due to this passing away of combustible matters in smoky furnace gases may reach as high as 30 per cent of the whole. A little consideration, however, will show that the loss of any large percentage of combustible matter, and consequently of heating-power, is quite out of the question. This may be proved in two ways—(1) by calculation of the two sources of heating-power as shown by an analysis of coal or dross used for steam-raising, and (2) by actual analysis of the furnace gases for combustible solids and gases.

In the following paper are given the results of these two methods of observation, the same dross being analysed and also employed as fuel in a works furnace, from which smoky gases were given off which were tested for combustible matters.

1. The following is the analysis of the dross employed :—

	Per cent.
Gas, tar, &c.	37·63
Fixed carbon	49·97
Sulphur	0·40
Ash	2·72
Water	9·28
	100·00
Heating-power (practical) due to gas, tar, &c.	1·16
" " " fixed carbon	6·49
	7·65

The points to be observed are the relative proportions of heating-power (represented in the analysis by the number of pounds of water at 212° F. capable of being evaporated to dryness by 1 lb. of the fuel) given out respectively by the combustion of gas, tar, &c., and by the fixed carbon. These are calculated according to Playfair's well-known formula, which was practically tested on coals intended for the British Navy, and which shows that while 1 lb. of fixed carbon is capable when burned of evaporating 13 lbs. of water at 212° F. to dryness, 1 lb. of the gas, tar, &c., will only evaporate 3·1 lbs. From these figures it appears that in the coal or dross the gas, tar, &c., only contribute 15 per cent of the total heat given out during the combustion, and that the fixed carbon produces the remainder, or 85 per cent. In coals with less of the former ingredients and more of the latter, which is commonly the case, the proportion given out by the volatile constituents would be considerably reduced. It is thus perfectly clear that even though the whole of the volatile matters (which can alone be accountable for any loss of combustible material) escaped combustion, there could not possibly be a greater loss of heat than 15 per cent of the whole, even in such an extreme case as this represents.

2. An analysis was made of the furnace gases given off during the burning of the dross, of which the results are given above, with the following results :—

	Gases very smoky. Per cent by volume.	Gases almost free from smoke. Per cent by volume.
Carbonic acid	5·0	3·5
" oxide ..	none	none
Hydrocarbons	trace	none
Nitrogen	79·9	79·9
Oxygen	15·1	16·6
	100·00	100·00

It has been asserted that carbonic oxide is given off in considerable quantity when much smoke is being produced, but it does not appear in this case; and Hempel, in his work on "Gas Analysis," comes to the conclusion that little or no combustible gases are present in furnace gases. In the volume referred to (page 205) Hempel says "furnace gases usually contain only carbon dioxide, oxygen, and nitrogen. All other gases are present in but very small amounts. In oft-repeated analysis the author has always found only traces of carbon monoxide, methane, and the heavy hydrocarbons." This is in complete accord with the analyses given above, and it may be taken for granted that the presence of carbonic oxide or other combustible gases in furnace gases is a most unusual occurrence. This is quite conclusive evidence that no appreciable loss of heat, even when the furnace gases are smoky, can be attributed to the passing away of the products of imperfect combustion in the gaseous form at least.

That there is loss of combustible matter in the smoke is an undoubted fact, but the quantity seems also to be greatly magnified in certain random statements. In the experiment referred to above the soot was also collected during one hour and a half with following results :—

	Grains per 100 cubic feet of furnace gases.
Carbonaceous matter..	30·81
Ash or mineral matter	20·65
Total soot	51·46

It will be observed that the soot collected consisted largely of mineral or incombustible matter. In several experiments to estimate the soot in furnace gases similar results to those were obtained, and the average would come very close to the quoted results of this special test.

To find how much carbonaceous matter was actually lost as smoke, it will be necessary to know the number of cubic feet of furnace gases given off by the combustion of, say, 1 ton of the dross. If the percentage of carbonic acid in the furnace gases is taken at 5 per cent, the total volume of these given off from 1 ton of dross would be about 940,000 cubic feet measured at the ordinary temperature and pressure, and this would contain 41 lbs. of carbonaceous matter and 27 lbs. of mineral matter. This would represent 1·83 per cent of the volatile matters (gas, tar, &c.) given in the analysis of the dross; and if from this is now calculated the heating-power according to Playfair's formula, it will only come to 0·057. This figure, compared with the practical heating-power (7·65) of the dross, goes to show that the solid combustible matter of the smoke can only account for the very small percentage of 0·74 of the total heating-power which can be obtained from the coal.

From the results of these experiments it is evident that the loss of combustible matters in smoke is very small indeed, and that the belief in immense loss by this cause is simply a fallacy, and it is decidedly not corroborated by experiment. In adopting methods of removing the smoke nuisance, it must therefore be borne in mind that there is little or no gain in burning smoke, and that other methods of dealing with the problem, such as Dulier's smoke absorption process, ought also to receive consideration.

THE IODONIUM BASES.*

By CHRISTOPHER HARTMANN and VICTOR MEYER.

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The iodonium iodide forms a beautifully crystalline addition product, obtained by stirring up the oxide with water and grinding briskly up with an alcoholic solution of iodine.

The chloride of the base forms very characteristic double salts with the mercuric, auric, and platinic iodides.

The sulphur compound of the iodonium bases are especially interesting. The iodonium compounds are distinguished by a remarkable resemblance to thallium hydroxide and its derivatives. The hydroxide and the carbonate are alkaline and readily soluble; the haloid compounds resemble the corresponding thallium derivatives in colour and solubility. This analogy raised the question whether the new bases might not form insoluble sulphides. This is, in fact, the case, and the substances formed are in aspect and general external nature deceptively similar to the recently precipitated sulphides of the heavy metals.

If a solution of the free base is mixed with yellow ammonium sulphide there appears a dense bright orange-red precipitate in large flocks, which if sufficiently concentrated causes the liquid to set into a paste. The precipitate is deceptively like recently precipitated antimony sulphide. If this experiment is performed at 0°, and if the liquid with the deposit is kept at this temperature, the new sulphide may be preserved for hours. At the temperature of a dwelling-room it is unstable. If the precipitation is effected at common temperatures, the phenomena are at first the same, but in a short time the precipitate in the liquid begins to hiss and throw out white clouds of vapour; it loses its solidity, and is changed in a few minutes into a mobile oil. This was taken up in ether, dried, and fractionated. Monobenzene iodide passed over first, then followed an oil boiling at a very high temperature, which was found to be a mixture of various phenyl sulphides, a fraction passing over from 300°—325° predominating.

This oil, $(C_6H_5)_2S_3$, was phenyltrisulphide. Hence the orange sulphide consists chiefly of trisulphide,—

$$(C_6H_5)_2I.S.S.S.I(C_6H_5)_2,$$

the formation of which is explained by the action of the yellow ammonium sulphide.

The normal sulphide, $(C_6H_5)_2I.S.I(C_6H_5)_2$, corresponding to the simple metallic sulphides, was obtained by means of sodium sulphide, Na_2S. If a solution of the iodonium base is mixed with a solution of this substance there is formed a bright yellow precipitate resembling in stability the compound just described.

The reduction of the free base in an aqueous solution with a 5 per cent sodium amalgam in the cold ensues according to the equation—

$$2(C_6H_5)_2IOH+4H=(C_6H_5)_2I.I+2C_6H_6+2H_2O.$$

A mol. of the base is thus resolved into benzene, water, hydriodic acid, which latter throws down a second mol. of the base as an insoluble iodide.

Iodonium Base as a By-product in the Production of Iodobenzenes.

A formation of the base in small quantities ensues in the preparation of iodobenzene from iodosobenzene with the aid of watery vapour. This reaction takes place most smoothly if the iodosobenzene is suspended in so much water as will be necessary at 100° to dissolve the iodobenzene to be subsequently formed. If after the complete decomposition of the iodosobenzene, the contents of the distillatory flask are allowed to cool, the iodobenzene is filtered off, the liquid concentrated to about one-third, and filtered again, we find in this filtrate a small quantity of the iodonium base along with the iodobenzene.

A number of further iodonium bases are being examined in the Heidelberg laboratory.

The general behaviour of the iodonium bases led to the question whether they are poisonous, and in how far they here resemble the thallium compounds. Dr. R. Gottlieb has kindly made a series of experiments in the Pharmacological Institute with diphenyliodonium hydrochlorate, and communicates the following results:—

The hydrochlorate of the base produces complete paralysis in frogs. It is of peripheric character, and effects a laming of the extremities of the motor nerves and of the substance of the muscles themselves. In this muscle-laming effect, even of a small dose (0·02—0·03 grm.), and by the simultaneous paralysis of the heart-muscle, the action of the base (in contrast to other organic iodine compounds) presents physiologically an analogy to some metals, *e.g.*, lead and thallium. On the other hand, its action upon the terminations of the motor nerves approximates to that of the ammonium bases.

The action on warm-blooded animals is more complicated. In addition to the peripheric lameness there ensues here central paralysis of the spinal marrow and of the *medulla oblongata*, so that doses of 0·03 per kilo. occasion death by the arrest of respiration.—*Berichte der Deutsch. Chem. Gesell.*

THE BOILING-POINTS OF DILUTE SOLUTIONS OF WATER IN ALCOHOL AND IN ETHER.

By C. E. LINEBARGER.

I.

No experiments seem to have been made with a view towards determining the boiling-points of water in alcohol with any considerable degree of precision. Certain authors, indeed, have made mention of some facts in regard to the points of ebullition and vapour tensions of mixtures of these two liquids, but their remarks cannot be said to be of much positive value. Having had occasion, as a preliminary to a physico-chemical research, to determine the points of ebullition of dilute solutions of water in absolute alcohol with all the accuracy that the present means of experimentation affords, and finding that the data obtained are not available in the aforesaid research, I communicate here the bare experimental results, since, as quantitative data, it may be of some use to place them on record.

The apparatus employed was Beckmann's ebullioscopic apparatus, modified as described in the Chemical News, vol. lxix., p. 279.

The water (freshly distilled) was weighed in small glass tubes (about an inch long), open at both ends and somewhat drawn out, so that their middle was narrowed considerably. Drops of water placed in such a tube are forced by capillary action to occupy the narrowed part, and are held there so firmly that the tubes can be placed in a vertical position without any water being lost. In the brief time required for the operation of weighing, no appreciable quantity is lost through evaporation. These tubes permit of the accurate weighing of quite small quantities of liquids which are but slightly volatile at ordinary temperatures. They are dropped down through

the condensing tube into the boiling solvent, and almost immediately a homogeneous solution results.

The alcohol made use of had been digested for some time at 50° to 60° C., with a large excess of freshly-burnt quicklime, and then distilled into a flask nearly half-full of fresh lime. This distillate was again distilled from the receiving flask into a flask provided with chloride of calcium tubes, to prevent access of moisture. The quantity required for an experiment was distilled over a little sodium from a flask provided with a distilling tube of three bulbs directly into the ebullioscopic tube, which had previously been very carefully dried. In this way it is believed that the alcohol may be reckoned as free from water as it has up to this time been obtained. As soon as the necessary amount of alcohol had passed over into the boiling tube, a tightly-fitting cork was fitted into it and the whole weighed, the tube plus cork plus heads having been tared beforehand. The cork was then removed, and the carefully dried thermometer put in position. Without delay the boiling-point of the pure alcohol was determined, and water was then added in the way described above. Two series of determinations were carried out in succession under the same atmospheric conditions. Immediately after the second series the ebullioscopic tube was filled afresh with alcohol, and its boiling-point determined in centigrade degrees with a carefully corrected thermometer divided into tenths of a degree. The readings of the boiling-points for the pure solvent on the Bechmani thermometer, in the two series of determinations, differed but 0·005° C., so that, for the arbitrary reading of the delicate thermometer, the reading on the other thermometer could be taken for the absolute boiling-point of the solvent.

Table I. contains the data of the experiments.

TABLE I.

Boiling-point of Alcohol under a Pressure of 756 m.m. = 78·1°.

Parts water in 100 parts alcohol.	Temperatures.	Parts water in 100 parts alcohol.	Temperatures.
m.	*t.*	*m.*	*t.*
0·241	78·090°	5·898	78·011°
0·876	78·078°	9·222	78·088°
1·810	78·053°	10·650	78·198°
2·443	78·009°	16·856	78·440°
4·497	77·990°	18·781	78·583°

If the above data be plotted in a curve with temperatures as axis of ordinates and parts water in 100 parts alcohol as axis of abscissæ, it is seen (what, indeed, is apparent enough from an inspection of the Table alone) that the addition of small quantities causes a lowering of the boiling-point of the alcohol, which attains a minimum when m is equal to 4·5. The boiling-point then rises regularly. At $m = 9·5$ the boiling-point of the solution is equal to that of the pure solvent, and for temperatures between 78·10° and 77·98° there exist two different concentrations of the solution, which have the same boiling-point.

II.

As a means of analysis of the amount of water of crystallisation given off at a certain temperature by hydrated salts, I determined the boiling-points of solutions of water in ethyl oxide up to the concentration where separation into two layers takes place. The apparatus and mode of operation were identical to those employed in the determination of the points of ebullition of dilute alcoholic solutions of water, only in this case, as ether does not attract very greedily moisture from the atmosphere, it was not necessary to take great precautions in the determinations to avoid contamination with water-vapour; it was not necessary to distil the ether directly into the ebullioscopic tube, &c.

The ether used had been "shaken out" at least twenty times with water, dried over fused calcium chloride, digested with mercury repeatedly until the metal was not further tarnished,* and finally distilled over phosphoric anhydride.

The results of the determinations are given in Table II.

TABLE II.

Boiling-point of Ether under a Pressure of 750 m.m. = 34·4°.

Parts water in 100 parts ether.	Temperatures.	Parts water in 100 parts ether.	Temperatures.
m.	*t.*	*m.*	*t.*
0·122	34·322°	0·657	34·158°
0·176	34·299°	0·821	34·128°
0·178	34·295°	1·092	34·098°
0·311	34·235°	1·320	34·074°
0·417	34·210°	1·326	34·070°
0·517	34·180°	(sat. sol.)	

There is a regular diminution in the boiling-point as the concentration increases until separation into two layers takes place. The observations of Marchis (*Comptes Rendus*, cxvi., 338, 1893) were not made with a thermometer delicate enough to detect the small difference in the boiling of pure ether and ether saturated with water, which, as seen from the Table, amounts to a little less than 0·3.

Paris, July 11, 1894.

CHINESE ALCHEMICAL LITERATURE.

By H. CARRINGTON BOLTON.

PROBABLY the most ancient treatise on alchemy now extant is the Chinese work entitled *Ts'an T'ung Ch'i*, of which the clearest modern commentary is by a scholar of the Yuen dynasty named Ch'en Chih Hsu. This treatise forms a small 8vo of 165 pages very poorly printed; my copy is a reprint issued during the reign of the present Emperor of China, Kuang Hsü.

Another curious alchemical work is that called *Wu chen pien*, composed by Chang Pih Tuan about 1075 A.D., in two volumes 8vo.

For copies of the above-named books I am indebted to John Fryer, LL.D., of Shanghai, the well-known translator of medical and scientific works into Chinese.

Little seems to be known concerning the contents of these and similar works; Dr. W. A. P. Martin, President of the University, Peking, has given a few extracts from *Wu chen pien* in his volume entitled "The Chinese" (New York, 1881), but these passages only stimulate a desire for more. Feeling sure that students of the history of chemistry would welcome a complete translation of the oldest treatise, *Ts'an T'ung Ch'i*, I have attempted to secure one at the hands of scholars. Only most profound Chinese linguists could make any attempt to solve the difficult problem, and I was fortunate enough to enlist the interest of two such experts. Miss Adèle M. Fielde, a resident of China for twenty-years, and the author of a Dictionary of the Swatow dialect, kindly began to examine the work with a view to translation, but finally abandoned it, feeling it could not be accomplished except in China with the aid of a native scholar. Thanks, however, are due to her for a serious effort.

Later I applied, through Dr. Martin, of Peking, to Lord Kingeast of Tseng, now attached to the Chinese Legation

* The mercury on being brought in contact with the ether tarnishes, and soon a black impalpable powder forms (sulphide of mercury?). The impurity which is thus removed by the mercury exercises a considerable influence upon the boiling-point of the ether. A sample of ether, washed and dried, boiled at 35·2° under a pressure of 743 m m.; after digestion with mercury the boiling-point was lowered to 34·3°. The ether employed in these experiments was of German fabrication; some ether bought in Paris does not show the same tarnishing of mercury.

the following manner. Taking the mixture of 4 c.c. of normal sulphuric acid and 40 c.c. of normal solution of sodium nitrate, let a drop be placed in each of two small porcelain basins, previously slightly warmed. To one of them let a single drop of distilled water be added, and then the herapathite test to both. In a few minutes the one which has received the drop of water will show well-marked crystallisations of herapathite, whilst the other will not show a trace.

The effect of dilution in changing the equilibrium of the solution of a base with mixed acids is thus made visible to the eye by a chemical reaction. Hitherto it has been a deduction from physical changes requiring great delicacy of measurement. Results of a precisely similar character were obtained when potassium bromide was substituted for sodium nitrate, and are no doubt of general occurrence.

The applicability of this method proved to be a good deal restricted, owing to the tendency of many acids when set free to decompose the herapathite reagent. For this reason the affinities of hydrobromic, hydriodic, chloric, iodic, and nitric acids could not be measured with accuracy, although many attempts, sometimes as many as thirty or forty or more, were made to get reliable results. This work, however, was not entirely thrown away. It demonstrated that *chloric acid* has the strongest affinity for bases of any known acids. It might have been expected *a priori* that a highly oxidised acid of chlorine would have stronger affinities than chlorine hydride. It also showed that the comparative affinity of nitric acid has hitherto been placed somewhat too high. Taking hydrochloric acid as 100, nitric acid scarcely exceeds 75.

The weaker acids, being for the most part without action on the test solution, give satisfactory results. Oxalic and tartaric acids, must, however, be excepted; the acid set free tends to form acid salts of sparing solubility, these are precipitated, thus the conditions are changed.

The results obtained are here tabulated:—

Hydrochloric acid	29·37	13·68	100
Succinic „	1·21	0·21	1·54
Acetic „	2·28	0·14	1·02
Citric „	1·02	0·53	3·87
Pyrophosphoric acid ..	0·963	0·926	6·77
Tungstic „ ..	1·2	0·2	1·46

The first column of this table shows the absolute number of molecules of the sodium salt which must be added without regard to the basicity of its acid in order that one molecule of sulphuric acid may be so completely saturated with base as no longer to give a reaction for free sulphuric acid.

In the second column these numbers are modified in such manner as to cause them to justly represent the comparative affinity of the acid. With monobasic acids the number of molecules is divided by 2, with quadrobasic acids it is multiplied by 2; for a tribasic acid it is multiplied by $\frac{3}{2}$. Bibasic acids only remain unchanged. Next, unity is subtracted because it is always the excess of the salt which must be present in order to keep the sulphuric acid saturated with base that gives the measure of the affinity of the acid. Were this correction not applied the entire result would be vitiated.

The third column gives the numbers as they appear when hydrochloric acid is taken at 100.

Instead of adding salts of different acids to sulphuric acid, we may add various acids to a salt formed by the union of sulphuric acid to a strong base—for example, to sodium sulphate.

Sulphuric acid is now recognised as being a weaker acid than hydrochloric, and yet we have seen that it is able to detach a certain quantity of base from a chloride. Further, that if the chloride is present in sufficient excess, the sulphuric acid may take up enough base to completely saturate itself. The general fact that a certain quantity of an acid may be expelled from a salt by another acid, even much weaker than the first, has been shown by the researches of Thomsen and of Ostwald. So that if, for example, we add acetic acid to a solution of sodium sulphate, a distinctly recognisable quantity of sulphate is decomposed and converted into acetate. A condition of equilibrium is produced in which the liquid contains both acids in a free state and both salts. In some way that we do not understand the presence of the free acid maintains the combined acid in its combination. The sodium acetate exists only by virtue of the free acetic acid present.

The existence of this state of equilibrium was first proved by Thomsen, who deduced it from the thermochemical changes which took place on mixing the solutions. Ostwald reached similar conclusions by making accurate determinations of the changes of volume, and consequently of specific gravity, which resulted from the mixing of the solutions, and in other ways.

In both these cases the conclusions are reached by logical deductions from the phenomena observed. But with the aid of the herapathite test the expulsion of sulphuric acid by a very much weaker acid can be rendered immediately evident to the eye. Thus, if to the solution of sodium sulphate we add acetic acid, and place two or three drops of the mixture in a warm porcelain basin and add some of the test liquid to it, in a few minutes we have a great number of small black rosettes of herapathite which crystallise out. Solution of sodium sulphate, not containing acetic acid, gives no such reaction with the herapathite test. It dries up to a pale yellow residue.

Acids vary very much in their ability to detach sulphuric acid from sodium. The following acids, when added to sodium sulphate and tested by the herapathite test, give the results here noted.

Malic acid gives an abundant crystallisation.
Succinic acid acts similarly.
Lactic acid, a moderate reaction.
Mucic acid, about the same as lactic.
Vanadic acid, traces.
Arsenic acid, abundant crystallisation.
Hippuric acid, distinct traces.
Salicylic acid, distinct crystallisation.

Of course the stronger organic acids—tartaric, oxalic, and citric—separate sulphuric acid with abundant crystallisations of herapathite when they are made to act on sodium sulphate and the test is applied. It was observed that an acid oxalate acts like a free acid. Thus when a solution of potassium binoxalate or quadroxalate is added to one of sodium sulphate, sulphuric acid is detached precisely as if free oxalic acid had been used.

It is clear that extremely weak acids, such as hippuric and salicylic, are able to take a certain quantity of base even from so strong an acid as sulphuric, setting free a recognisable quantity of this latter acid. Carbonic acid is still weaker than these. Ostwald, in determining the relative affinities of acids by the rate of the decomposition of acetamide and by the inversion of cane-sugar, found no appreciable effect from carbonic acid. It therefore became of interest to ascertain if any sensible decomposition of sodium sulphate would result from the action of this acid.

Perfectly pure carbonic anhydride was passed for a long time through a solution of sodium sulphate without setting free a recognisable trace of sulphuric acid. This was expected; the experiment was only preliminary to its repetition under pressure.

For this purpose sodium sulphate, with the test solution, was placed in one leg of a bent tube; in the other leg was placed sodium bicarbonate; and the tube was sealed. Heat was gradually applied to the bicarbonate. In the second trial the pressure was raised so high that the stout glass tube was ultimately shattered wi h

violence. The leg containing the test liquid and sulphate had been secured in a clamp and remained uninjured. The liquid therefore had been subjected to the action of carbonic anhydride at a high pressure; it, however, gave no indications of a separation of traces of sulphuric acid under its action. It is to be remarked that this test is more decisive than if a solution of sodium sulphate had been used and had been tested afterwards. For in this last case, on release of the pressure, the reaction might readily be reversed with re-combination of sulphuric acid, had any been liberated. But with the test liquid present during the pressure this reversal could not take place.

Carbonic anhydride, therefore, does not even under pressure set free any portion of sulphuric acid from sodic sulphate.

The reactions described in this paper indicate:—

(1.) That when to free sulphuric acid a salt is added in sufficient quantity to cause the whole of the sulphuric acid to saturate itself with the salt-base, it is possible by means of the herapathite test to determine the exact point of such saturation. At this point there will necessarily be as much of the acid at first combined with the base, now free in the solution, as corresponds to one molecule of a bibasic acid, that is two of a monobasic acid, half a molecule of a quadrobasic acid, &c. From this we can deduce the exact nature of the resulting equilibrium.

(2.) That a series of equilibria thus obtained with different salts enables us to determine the comparative strength of the affinities of the acids of those salts.

(3.) That the fact, already proved in other ways, that even small quantities of weak acids, added to sulphates, will set free a certain quantity of sulphuric acid, can by means here given be for the first time rendered visible to the eye by a well-marked chemical reaction.

SEPARATION OF ZIRCONIUM BY MEANS OF SULPHUROUS ACID.

By CHARLES BASKERVILLE.

WHILE testing the accuracy of the various methods recommended for the estimation of zirconium, I was led, because of the analogy of the elements, to try a method commonly used with titanium; viz., prolonged boiling of a potassium bisulphate fusion in dilute solution with sulphurous acid in excess. On application of this method, however, on a solution of zirconium sulphate (prepared by dissolving the hydroxide in sulphuric acid), I failed even after boiling four hours with an excess of sulphur dioxide to obtain a precipitate, if the solution was acid. If the solution was nearly neutralised with ammonium hydroxide and then boiled with an excess of sulphur dioxide, after being greatly diluted, a precipitate was produced. This precipitation, however, was incomplete, even after boiling six hours or passing steam through the same for two or three hours. The precipitate too was very finely divided, running through all filter papers at my command. Therefore this method could not be used.

But on addition of sulphurous acid to a solution of zirconium chloride, even in a cold acid solution, a dense white precipitate was immediately noted. On boiling with an excess of sulphurous acid in a neutralised solution, *i. e.*, the hydrochloric acid solution neutralised by ammonium hydroxide until the slight precipitate formed was no longer dissolved on boiling, and this precipitate then taken up with two or three drops of dilute hydrochloric acid, the zirconium was completely precipitated.

The accuracy of the method is seen in the following results:—

	Found.	Used.
ZrO_2..	0·1074	0·1077
„	0·1078	0·1077
„	0·1043	0·1038
„	0·1070	0·1077
„	0·1047	0·1050

The precipitation took place immediately on addition of sulphurous acid, and after two minutes boiling the precipitate settled quickly and was easily filtered.

This method then is applicable to the chloride only, and a sulphate would have to be first changed into chloride by precipitation with ammonium hydroxide and resolution in hydrochloric acid. The presence of large amounts of such salts as ammonium chloride did not aid the precipitation of the sulphate. The presence of free hydrochloric acid must be avoided, and it is best to use a fresh solution of sulphurous acid or the sulphur dioxide gas direct.

This method affords an excellent means of separating zirconium from iron. Several experiments were carried out upon solutions containing known amounts of the chlorides of these two metals. The zirconia was precipitated by sulphurous acid, boiled five minutes, and washed four or five times with hot water. The iron was titrated in the filtrate.

The experiments resulted as follows:—

	Found.	Used.
ZrO_2..	0·1074	0·1070
Fe	0·0825	0·0823
ZrO_2..	0·1078	0·1070
Fe	0·0820	0·0823
ZrO_2..	0·1043	0·1043
Fe	0·0439	0·0423

This method served for the separation of zirconium and aluminium as well, as may be seen by the following results:—

	Found.	Used.
ZrO_2..	0·1042	0·1043
Al_2O_3	0·0608	0·0610
ZrO_2..	0·1070	0·1070
Al_2O_3	0·0316	0·0305

—*Journal of the American Chemical Society*, xvi., No. 7.

THE CENTENARY ANNIVERSARY OF THE BIRTH OF FRIEDLIEB FERDINAND RUNGE.

THE discoverer of aniline was born in 1794 at Billwärder, and died at Oranienburg in 1867. In his 17th year he discovered accidentally the action of certain organic bases on the iris of the eye. This observation, which he followed out by experiments upon cats with belladonna, hyoscyamus, and datura, attracted the attention of Prof. Doebereiner, who introduced the young student to Goethe, then almost supreme in the German intellectual world.

In 1818 Runge graduated at Jena as M.D. with a dissertation on belladonna. His dissertation on appearing as a candidate for the degree of Ph.D. was on indigo. He became a "privat docent" in the University of Breslau, and formed an intimate acquaintance with H. Milde, the proprietor of a celebrated tissue-printing establishment at the Ohlau-Gate. At this time Runge came forward as a bitter opponent of everything un-German in language and customs. It is not strange that a man whose youthful impressions dated from days when Germany groaned under the yoke of the first Napoleon should be an enemy of France. But, like the poet Heine, and the distinguished naturalist Buchholz, he seems to have been especially hostile to England. In his book on the production of a guano from German materials, he speaks of the import-

ance of spoiling the game of the English and their assistants.

His principal works were on the colouring matters of madder, on madder-dyeing, on the chemistry of colours (*Farbenchemie*), and on the products of the distillation of coal-tar.

His discovery of aniline—or, as he named it, kyanol—among the products of coal-tar took place in 1833, or, according to Prof. Dr. Wagner, in 1834, and ensured his celebrity. During the same series of researches he discovered carbolic acid and rosolic acid. He also invented a method of purifying the German graphite so that it might compete with that imported from England.

He obtained palmitin from palm oil, and made from it palm-oil candles. In 1841 he discovered paraffin in peat-tar. His last years were devoted to the production of artificial manures, but with no decisive success.

As regards his capital discovery, that of aniline, he found an obstinate opponent in Dr. Reichenbach. Not until ten years later were Runge's claims successfully enforced by Prof. A. W. von Hofmann.

In spite of his high endowments and his originality, there was in his composition, as Prof. A. von Hofmann admits, something which hindered him from becoming a successful man and the creator of an epoch in science. This "something," as we are informed by H. Suppe (the author of the documents before us), was to a great extent the readiness with which he communicated his ideas to others without taking any steps to secure his own rights.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 21st, 1894.

Dr. Armstrong, President, in the Chair.

(Concluded from p. 47).

39. "*The Preparation of Sulphonic Derivatives of Camphor.*" By F. Stanley Kipping, Ph.D., D.Sc., and William J. Pope.

The method which the authors have previously given (*Trans.*, 1893, 548) for preparing the sulphonic chlorides of camphor and of its halogen derivatives, by acting on the sodium salts of the sulphonic acids with phosphorus pentachloride, is tedious and uneconomical. The crude hygroscopic sodium salts do not crystallise from the impure solutions in which they are obtained after sulphonation, and during the process of drying they undergo partial decomposition; the resulting sulphonic chlorides are consequently very impure, and are only isolated with difficulty, the yield being comparatively small.

Requiring large quantities of the pure sulphonic chlorides in order to study the halogen deirvatives of camphor, which may be obtained from them by the method indicated in a previous note, it seemed desirable, in the first place, to improve the mode of preparation. This was accomplished by employing the ammonium salts of the sulphonic acids, which, unlike the sodium salts, are anhydrous, crystallise comparatively readily, and are easily obtained in a pure condition, even from highly impure solutions. The crude sulphonic chlorides prepared from these salts contain but little impurity and are very easily isolated, the yield being nearly theoretical; the sulphonic bromides, which were very difficult to obtain from the crude sodium salts and phosphorus pentabromide, may be readily prepared from the pure ammonium salts.

Bromocamphorsulphonic bromide, $C_{10}H_{14}OBr\cdot SO_2Br$, prepared from ammonium bromocamphorsulphonate, crystallises in large transparent lustrous octahedra, and is quite different in crystalline form from the corresponding sulphonic chloride; it has no definite melting-point, but decomposes at about 140° with evolution of sulphur dioxide, forming a new *dibromocamphor*, which will be described later.

Chlorocamphorsulphonic bromide, $C_{10}H_{14}OCl\cdot SO_2Br$, obtained from the ammonium salt of chlorocamphorsulphonic acid, also forms large colourless octahedra and undergoes decomposition when heated, giving a halogen derivative, which is being investigated.

Camphorsulphonic bromide, $C_{10}H_{15}O\cdot SO_2Br$, was prepared from the feebly active ammonium camphorsulphonic acid, as it was interesting to compare its behaviour with that of the inactive sulphonic chloride (*Trans., loc. cit.*); the crude product seems to consist of a mixture of optically active and inactive substances, as in the case of the sulphonic chloride, but the existence of a definite racemic modification has not yet been established.

40. "*Dextro-rotatory Camphorsulphonic Chloride.*" By F. Stanley Kipping, Ph.D., D.Sc., and William J. Pope.

Dextro-rotatory camphorsulphonic chloride has been previously described, but owing to the great difficulty experienced in separating even a few grms. of this substance from the inactive modification, it was not possible to make as complete a study of its derivatives as appeared desirable. It has now been ascertained that this optically active sulphonic chloride may be prepared in almost any quantity from the ammonium salt of bromocamphorsulphonic acid; when the latter is reduced with zinc-dust and ammonia, it is rapidly converted into the ammonium salt of dextro-rotatory camphorsulphonic acid, from which the sulphonic chloride may be obtained by acting with phosphorus pentachloride (see preceding note). The product crystallises in colourless transparent tetrahedra melting at 137·5, and is shown to be identical with the optically active sulphonic chloride already described, not only by these properties but also by crystallographical measurements. Its production in this way not only makes it possible to push the investigation of its derivatives further, but is also of theoretical interest, inasmuch as it proves that on sulphonating either camphor or bromocamphor the sulphonic group becomes united with one and the same carbon atom, unless the highly improbable assumption be made that camphor contains two similarly orientated groups from which hydrogen may be displaced.

Dextro-rotatory camphorsulphonic bromide,—

$$C_{10}H_{15}O\cdot SO_2Br,$$

has also been prepared in a similar manner; it crystallises in well-defined transparent octahedra, isomorphous with the crystals of the active sulphonic chloride, and resembles the latter very closely in ordinary properties.

The halogen derivatives obtained by heating these two active compounds will be described later.

41. "*On the Combination of Chlorine with Carbon Monoxide under the Influence of Light.*" (Preliminary Notice). By Gibson Dyson, Ph.D., and A. Harden, Ph.D., M.Sc.

Equal volumes of chlorine and carbon monoxide were mixed by diffusion in an apparatus consisting of two cylindrical bulbs with water jackets, connected by a capillary tube with a gauge containing sulphuric acid, the space above the acid being filled with carbonyl chloride, so that only the two gases and the product of their combination were present.

The action of light upon the mixed gases was studied by burning a measured piece of magnesium ribbon at a constant rate and at a measured distance in front of one of the bulbs, and observing the movement of the acid in the gauge. As soon as equilibrium was restored, a second piece of magnesium was burned, and the gauge again observed. It may be assumed that in these experiments rise of the acid in the capillary tube of the gauge is proportional to the amount of combination produced. The ex-

periments hitherto carried out show that when a mixture of equal volumes of the two gases, half saturated with moisture, is exposed to the action of the light from burning magnesium ribbon, there is a *well-marked period of photochemical induction*.

This is illustrated by the following numbers, taken from one of our numerous experiments, which give the rise of the acid in the gauge in scale divisions caused by successive equal amounts of light.

	Scale Divisions.
1	1
2	8·5
3	18
4	20
5	24
	Constant.

The action of light upon exactly equivalent volumes of the two gases under various conditions is now being investigated, and experiments are being made on the combination of chlorine with other gases. We hope at no distant date to be able to lay the results of these experiments before the Society.

42. "*Solution and Pseudo-solution.*" Part II. By S. E. Linder and Harold Picton.

This is a continuation of previous work by one of the authors on arsenious sulphide solutions. The previous series of arsenious sulphide solutions has been extended, a solution having been prepared by the action of sulphuretted hydrogen on more dilute arsenious acid, which is filterable through a porous pot in addition to being diffusible. The following different solutions have now been prepared:—As_2S_3 (α), with aggregates visible under microscope; As_2S_3 (β), invisible, but not diffusible; As_2S_3 (γ), diffusible, but non-filterable; As_2S_3 (δ), diffusible and filterable, but showing a polarised beam in Tyndall's experiment.

The following experiments have been made with the "higher grade" solutions (γ and δ).

1. *Coagulative Power.*—Metallic salts are found to arrange themselves in sharply-divided groups as regards their power of coagulating solutions of arsenious sulphide. The group into which a metallic salt will fall depends on the valency of the metal. The trivalent metals have the highest coagulative power, divalent metals about one-tenth, and monovalent metals less than one five-hundredth of this power. These differences are also shown by the same metal (*e.g.*, iron) when exhibiting varying valencies. The negative group also causes variation, and it is noteworthy that the coagulative power of the halogens is very similar, and so, also, is that of the arsenic and phosphoric acid radicals.

The effect of successive additions of salts of the same group is a corresponding increase in the amount of coagulation, whilst that of salts of different groups is to hinder coagulation, the latter effect attaining a maximum when a certain quantity of the first salt has been added. Thus if potassium chloride is first added and then strontium chloride, the addition of more potassium chloride increases up to a certain maximum the amount of strontium chloride required to complete the coagulation.

Certain applications of these results have suggested themselves. Thus, coagulative power might possibly be applied to check the valency of a metal in different compounds. Again, it is noteworthy that there is an unusual difference between the coagulative powers of free arsenic and phosphoric acids and their salts. It is also suggestive that free sulphurous acid differs widely in coagulative power from sulphuric acid, while sodium sulphite differs only comparatively slightly from sodium sulphate. Possibly relative coagulative powers may have an interesting bearing on questions of constitutional relationship.

2. *Relative Density.*—This varies quite regularly with dilution, the relation between relative density and dilution being represented by a straight line. This agrees with the results obtained with fairly dilute sugar solutions (9 per cent), while strong sugar solutions (18 per cent) and dilute salt solutions (0·2 per cent) show a smaller diminution of relative density indicative of the formation of hydrates.

3. *Volume-change on Coagulation.*—It is found that when coagulation is conducted in a very sensitive apparatus, consisting of a flask of about 350 c.c. capacity, fitted with a ground stopper carrying a capillary tube, there is absolutely no volume-change on coagulation. Calcium chloride was used as the coagulant, and to eliminate the contraction produced by it, equal quantities of the same solution were used inclosed in thin glass bulbs. Two determinations with distilled water gave a volume change of 0·0177 and 0·0174 c.c. With the sulphide solution the contraction was 0·0175 c.c.

4. *Surface Tension.*—As determined by the rise of the solution in a capillary tube, the surface-tension of water is unaffected by the presence of dissolved arsenious sulphide. Cane-sugar, on the other hand, causes a small but distinct increase of surface-tension.

5. *Osmotic Pressure.*—The results of osmotic pressure measurements are very variable, but the authors think themselves justified in concluding that an osmotic pressure exists. Thus, a 4 per cent solution has yielded a pressure of 17 m m. of water. No comparative determinations seem reliable, but a distinct pressure is always observed with diffusible solutions, but this is not observed with filterable substances. The smallness of the pressure would suggest exceedingly great molecular complexity.

Among new solutions examined may be mentioned the uranium and iron dextrosates, kindly placed at our disposal by Mr. Chapman; these scatter light and are non-filterable, but the iron compound, in presence of ammonia and ammonium chloride, does not scatter light and is filterable.

The complicated tungstate,—

$$60WO_3{\cdot}3P_2O_5{\cdot}V_2O_5{\cdot}VO_2{\cdot}18BaO+150H_2O,$$

does not scatter light and is filterable.

43. "*Solution and Pseudo-solution.*" Part III. By Harold Picton and S. E. Linder.

The authors describe further work on the electrical repulsion of certain solutions. The results are fully tabulated in the paper. It may be well to recall that if an attempt is made to pass a current through arsenious sulphide solution, the sulphide is repelled as a whole from the negative electrode, and also to a certain extent from the positive electrode, without appreciable electrolysis. A large number of solutions showing characteristic repulsions have now been investigated; thus aniline blue (of various kinds) is repelled from the negative electrode, Magdala red and methyl violet from the positive, sulphur and iodine are repelled from the negative electrode.

It seems impossible to obtain repulsion in an absolutely non-conducting medium. For instance, iodine in carbon disulphide is not repelled. Again, on doubling the length of an arsenious sulphide column, the rate of repulsion is approximately halved. Indigo in water is repelled from the negative, in naphtha it is not repelled.

In general, when solutions exhibiting opposite repulsions are mixed, complete coagulation of the dissolved substance occurs. Under certain conditions of dilution, the coagulation may be avoided, but in this case the mixture descends to a lower "grade" of solution. The aggregates of this "lower grade" solution are repelled as a whole from one electrode. Further, in two suitable cases the experiment was made of adding a new solvent (alcohol). The aggregates of the "lower grade" mixture were then found to dissociate and to be repelled individually from their characteristic electrodes. These facts are all illustrated by the cases of aniline blue mixed with Magdala red, and aniline blue mixed with methyl violet. Aqueous solutions of aniline blue with weak alcoholic Magdala red coagulate; aqueous aniline blue with aqueous Magdala red yield a "lower grade" solution, which is repelled from the negative electrode unless the Magdala red

is much in excess. On dissolving the coagulation of (1) in strong alcohol, a higher grade solution is obtained, in which the aniline blue and Magdala red are repelled separately.

If a degraded solution of two oppositely repelled substances is taken, *e.g.*, an aqueous solution of aniline blue and methyl violet, on adding a third substance (*e.g.*, ferric hydrate) the combined aggregates in the solution are carried down as wholes, and the result is that all three substances separate out. On the other hand, if we take an alcoholic and dissociated solution of aniline blue and methyl violet, on adding ferric hydrate (positive) only the aniline blue (negative) is carried down, while the methyl violet (positive) is left in solution. This affords an additional test of "degradation" where the optical test fails. Thus aniline blue in alcohol with ferric hydrate in alcohol do not combine, for on coagulating with potassium sulphate only the ferric hydrate is carried down. The aqueous solutions do combine, as is shown by the potassium sulphate causing both to separate. Filtration also affords a test of combination. Thus arsenious sulphide (positive or negative) does not coagulate with aniline blue (negative), but combination occurs, as on filtering no aniline blue passes through the porous pot.

OBITUARY.

C. R. ALDER WRIGHT, B.Sc. (Vict.), D.Sc. (Lond.), F.R.S.

Chemists will hear with deep regret of the death of Dr. C. R. Alder Wright, whose reputation as an ardent and thorough investigator in the field of chemical and physical science has grown collaterally with fully equal distinctions won in the application of the science to industry.

No English chemist has covered so much ground. His work begins with a paper published in February, 1866, in the *Journal of the Chemical Society*, on the "Action of Light on Sensitive Photographic Papers," when Wright was a student at Owens' College, Manchester.

Leaving Owens' College, he entered the Weston Works of the Runcorn Soap and Alkali Co., Lim., as chemist, and successor to Mr. J. W. Kynaston.

In August, 1867, we find a valuable paper in the *Journal of the Chemical Society* in which Dr. Wright describes his experiences in alkali works.

We next find him as private assistant in the laboratory of St. Thomas's Hospital, and about this period some letters appear in the columns of the Chemical News from his pen on the subject of methods then in vogue for testing alkalis, and on kindred subjects of technical interest.

His work comprises investigations of simple substances like hydriodic acid, and some of the most complex substances, like the vegeto-alkaloids, upon which he laboured for many years—sometimes alone, and sometimes in conjunction with Matthiessen and others. These researches deserve to be called classical if any researches do, and they occupy an entire department of organic chemistry—they fill a thick volume.

Alder Wright was a mathematician as well as a chemist, and we find nine papers "On the Determination of Chemical Affinity in terms of Electromotive Force." These papers alone occupy another thick volume. They appeared for the most part in the *Phil. Mag.*

In the *Journal of the Chemical Society* for Feb., 1873, there is a paper "On the Hydrogen Occluded by Palladium," by W. Chandler Roberts and C. R. A. Wright. A series of papers then follows on "Isomeric Terpenes," Essential Oils," &c., in the same year.

On Friday, March 13, 1874, Wright delivered an evening lecture at the Royal Institution "On the Chemical Changes accompanying the Smelting of Iron in the Blast-furnace," embodying extensive experience he had gained in the works and research laboratory of Sir Lowthian Bell.

In the *Journal of the Chemical Society*, Jan., 1878, appeared his first paper entitled "Researches on some Points in Chemical Dynamics."

The fourth of these papers appeared in December, 1880. In January of the same year a paper was communicated by Wright on "Notes on Manganese Dioxide."

The foregoing is a very inadequate summary, and readers of the Chemical News may convince themselves how inadequate it is by referring to its pages during the last thirty years. His voluminous and valuable work on "Ternary Alloys" was communicated to the Royal Society during the years 1889 and 1892. His work on Soap formed the subject of the Cantor Lectures to the Society of Arts. Besides this, we are conscious of many omissions as regards investigations of technical interest, such as the "Cuprammonium Compounds and their Applications," "Certain Voltaic Combinations," "Aluminium Alloys," &c., &c. It is not generally known that Wright received a preliminary training as an Engineer. He was at first designed for that profession by his father.

During the last week or two his health had been somewhat failing through an attack of *diabetes mellitus*, but no consequences of serious import were anticipated until Monday, July 23rd. On the Wednesday morning he became comatose, and never recovered consciousness until death set in early in the afternoon of that day, July 25th. He was forty-nine years of age.

CORRESPONDENCE.

THE LAW OF GASEOUS MIXTURES. A RECLAMATION OF PRIORITY.

To the Editor of the Chemical News.

Sir,—It has only recently come to my knowledge that Mr. J. A. Wanklyn had published in the Chemical News (vol. lxv., p. 122, March 11, 1892), a paper in which he asserted that he had found, more than thirty years ago, a law concerning the mixture of gases. In reference to this law, according to which the total volume of a gaseous mixture is equal to the sum of the volumes of the constituents taken under the same pressure, he said that a "detailed proof" would be found in a memoir published jointly by Sir Lyon Playfair and himself in the *Trans. Roy. Soc. Edin.*, xxii., Part 3, 1861. He also said that this proof had, however, escaped attention entirely. Now I may be allowed to remark as follows:—

1. The same law was pointed out, in the most explicit manner, in a book published by my father and myself in March, 1886, and bearing the title "Neue Grundgesetze zur rationellen Physik und Chemie," von Dr. E. Dühring und Ulrich Dühring (Zweite Folge, Liepzig, O. R. Reisland). Moreover, in the same book, namely, in its fifth chapter, of which I am the sole author, I proved this law for atmospheric air (as a mixture of nitrogen and oxygen) at various pressures up to 1354 atmospheres, by means of tables of verification, the basis of which were the experimental data due to Messrs. Natterer and Amagat (pp. 3 to 5). Then I was led by some theoretical considerations to declare it applicable to each state of matter, but with the restriction that the cohesion between the heterogeneous particles of the mixture be neither increased by a sort of chemical attraction between the constituents ("Mischungsaffinität") nor exceeded by the statical effects of the disaggregation of homogeneous particles (p. 22); otherwise I should have been in contradiction to the best founded theories concerning the nature of solutions

and liquid mixtures. The examples of dilatation accompanying mixture of gases being unknown at that time, I could not refer to them in pursuing my view of the uniform nature of all sorts of physical mixtures; but I said that in the cases of mixtures formed with contraction, the fundamental law of partial volumes does, however, apply, provided that it be combined with a modifying law relative to the action of mixing—affinity (p. 12). Besides, I laid the greatest stress on the fact that my law of partial volumes, whether exact or approximate, represents, by reason of the deviation of every gas from Mariotte's law, a decisive counter-argument against Dalton's hypothesis of real partial pressures (pp. 4 and 23). In order to confirm that all these things are really contained in the "Neue Grundgesetze, &c.," I call attention to the heading of its fifth chapter, "Neue Theorie der Gasmischungen. Gesetz der Partialvolumina." The table of contents for its first number reads thus: "Falschheit eines angeblichen Gesetzes der Partialdrucke. Zurückgreifen auf die strengen hydrostatischen Gesetze. Kurze rechnungsmässige Darlegung der Unrichtigkeit der bisherigen Vorstellung aus den beobachteten Thatsachen. Im Gegensatz hiezu das Gesammtvolumen des Gemisches als Summe der eignen Partialvolumina der Bestandtheile." These quotations will, I think, be sufficient of themselves, the respective passages being too long to be copied *in extenso* in the present letter.

2. The passage quoted by Mr. A. Wanklyn (CHEMICAL NEWS, vol. lxv., p. 122), as taken from the memoir read before the Royal Society of Edinburgh, on the 29th of April, 1861 (*Transactions*, pp. 458—465) is affected with a curious misplacement of the mark of quotation, which alters the sense *just at the most decisive lines*, viz., the ultimate period included within the marks of quotation ("In short, there is the most varied evidence that, so long as there is no actual chemical action between the molecules by a gaseous mixture, the fact of the molecules being dissimilar has no influence upon the volume") *is not to be found* in the ancient memoir of Messrs. Playfair and Wanklyn.

3. This ancient memoir was by no means intended to demonstrate or to confirm a law of partial volumes, but, on the contrary, *to found on an opposed principle* the superiority of a new method for determining vapour-densities. Indeed, as every reader would become aware by perusing that memoir, the authors went upon the assumption that the (partial) volume of a vapour when diluted with a "permanent" gas must, by reason of the diminished cohesion between the particles of the vapour, be *greater* than the volume of the non-diluted vapour measured under the same pressure. Accordingly, they held that the vapour-density, being elsewhere increased by the mutual actions between less separated particles, must, by effect of the dilution, approach more nearly to the so-called theoretical density; thus their vapour-density methods bore upon a generalisation of the fact that in many cases of mixing gases or vapours, there was observed increase in volume by the action of molecular disaggregation.

However, as I believe that the majority of such readers as take view of the present letter have not at hand the above cited volume of the Edinburgh *Transactions*, I think it may be useful to extract from that memoir several passages *verbatim*. After having rejected the method of Gay-Lussac as being little practical for determining vapour-densities at feeble pressures, the authors said (p. 443): "The second remedy to which we have alluded, viz., the separation of the particles of the vapour by a considerable excess of a permanent gas, having in itself a normal coefficient of expansion, such as hydrogen or air, appeared to be one which promised good results, and has chiefly engaged our attention—especially so, because it offered a means by which both the difficulties to which we have alluded might be overcome—viz., the danger of incipient condensation on the surface of the containing vessels, and the danger of contraction by the action of cohesion when the particles of gas approach each other too closely. The first danger can be wholly avoided by always having an excess of gas, so that it does not become saturated with the vapour under examination. The second danger is also greatly reduced by the admixture of the gas; for we shall show, by experimental evidence, that, although the coefficient of expansion of a vapour taken under ordinary circumstances, is higher than that of air, it undergoes an alteration when the vapour is mixed with hydrogen gas—this alteration making it, if not identical, at least approach closely to that of air and other non-condensible gases." After this, Messrs. Playfair and Wanklyn gave an account of their investigations concerning the vapour densities of alcohol and ether, and yielding the result expressed in the following terms (pp. 448—449): "We have shown that the specific gravity of either of these vapours is lower when taken in presence of hydrogen than when taken alone." . . . "It follows, therefore, that hydrogen hinders the contraction of alcohol and other vapours; in other words, it diminishes the expansion coefficient of these vapours.

"The differences observable between the two sets of specific gravities are small, but they are constant—just, in fact, what might be expected." In reference to the case of a gaseous mixture of one volume of ammonia with two volumes of steam, prepared at 100°, which Mr. Wanklyn marked, thirty-one years later, as the most suitable example to verify the law of partial volumes, although there was recognised a contraction by $\frac{1}{15}$th of the total volume—I remark that the purpose of the experiment in question was only an exploration whether in this case some chemical influences do exist or not. The truth of my assertion will be seen clearly from the following lines (p. 465), which I quote literally: "Another illustration of the vapour-density methods above described consists in an inquiry into the existence of hydrated oxide of ammonium.

"Can hydrated oxide of ammonium exist at 100° C., and in the gaseous state? To solve the problem, a quantity of dry ammonia" . . . "Therefore, at 100° C., ammonia and aqueous vapour can exist side by side without suffering any considerable contraction."

The comparison of this latter passage with the statements contained in Mr. Wanklyn's recent paper will alone be sufficient to enable a want of conformity to be recognised. As we find such a want in all passages, we must assume that no claim of priority relative to the law in question can be maintained by Mr. Wanklyn by appealing to his former paper; and as his recent paper was written *six years after* I had published my discovery, it must be concluded that the priority is thoroughly on my side.

Pray have the kindness to publish this letter of claim and rectification in your esteemed journal.—I am, &c.,

ULRICH DÜHRING.

Neuendorf, near Potsdam, Germany,
July 29, 1894.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxix., No. 2, July 9, 1894.

At the sittings of the Academy the President announced the death of M. Mallard, a member of the Section of Mineralogy. The late *savant* died on July 6th after a very brief illness, and was buried on July 9th.

On the Photographs of the Moon obtained with the Great Equatorial of the Paris Observatory.—MM. Loewy and Puiseux.—Whilst doing justice to the work of

Dr. Weineck we may be permitted to believe that his decision is open to appeal. Our experiments lead us to think that a photographic enlargement, executed with care, of the dimensions foreseen in Mr. Langley's project renders easily visible all the details whose existence on the proof can be affirmed.

New Derivatives obtained from Benzoylbenzoic Acid.—A. Haller and A. Guyot.—The researches of the authors have been effected by the elegant method of Friedel and Crafts by treating a mixture of phthalic anhydride and of benzene with aluminium chloride. If we use pure benzene, free from thiophene, we may obtain 92 per cent of the theoretical yield. The compounds obtained and studied are diphenylphthalide, dimethylamidodiphenylphthalide, with its hydrochlorate, which, if oxidised, gives a feeble violet colouration, dimethylamidotriphenylmethanorthocarbonic acid, and dimethylamidophenylanthranol.

Experimental Production of the Contagious Peripneumonia of Oxen by means of Cultures. Demonstration of the Specific Character of Pneumobacillus liquefaciens boris.—S. Arloing.—The author's experiments enable him to affirm decisively that the virulent agent of contagious peripneumonia is an ordinary microbe, and that this microbe is the *Pneumobacillus liquefaciens boris.*

Comparative Researches on the Products of Combustion of Coal-Gas yielded by an Argand Burner and by an Auer Burner.—M. Gréhaut.—This paper will be inserted in full.

New Cobalt Colours.—M. Bérand.—The author laid before the Academy some specimens of new colours extracted from cobalt. No particulars are given either of their characters or of their preparation.

Special Images of the Sun given by the Simple Rays, corresponding to the Black Rays of the Solar Spectrum.—H. Deslandres.—This paper will be given in full.

Thermic Radiations comprised in the Luminous Portion of the Spectrum.—M. Aymonnet.—The following conclusions are deducible from the author's observations:—1. The eye does not perceive all the radiations comprised between the red and the violet. 2. The eye is not affected by the radiations intercepted by water. 3. If the medium interposed between the radiant source and the apparatus for measurement contains water there is an agreement—though imperfect—between the distribution of heat and that of light in the same region of the spectrum. 4. The brilliant rays or bands which we may observe in a spectrum are only those or a part of those which pass through water. Thus it is probable that sodium emits in R–V other radiations than the D rays. 5. Since water intercepts the obscure rays its absorption spectrum is discontinuous in λ; it is very probable that this holds good for the absorption spectra of all substances; none of them is continuous.

Relation between the Specific Gravity of a Saline Solution and the Molecular Weight of the Salt Dissolved.—Georges Charpy.—The density of a saline solution increases in proportion to the molecular concentration if we admit that the molecular weight of water at 0° is about 3 × 18. The densities of solutions of analogous salts equally concentrated are approximately proportional to their molecular weights.

Syntheses by means of Cyanacetic Ether. The Phenacylcyanacetic Ether.—T. Clobb.—The diagnosis of these ethers is very easy. The mono-substituted ethers turn yellow in contact with aqueous potassa. After solution the liquid gives a blue precipitate with acids. The bi-substituted ethers, on the contrary, dissolve in alcoholic potassa with a deep blue colour, and form a red precipitate on acidification.

On Paraphthalodicyanacetic Acid.—J. Locher.—This paper is not adapted for useful abstraction.

On the Tar of the Pine.—Adolphe Renard.—The tar contains about—

Water	3·5
Hydrocarbons, volatile, below 300°	12
,, ,, between 300—360°	45
Phenols	18
Pitch rich in retene	21·5

Habituation of Ferments to Antiseptics, and Influence of such Habituations on their Chemical Action.—J. Effront.—This paper will be inserted at considerable length.

MISCELLANEOUS.

Professor von Helmholtz.—Our readers will learn with regret that this illustrious physicist was last week seized with paralysis of the left side.

Probable Value of the Atomic Weights Deduced from the Researches of Stas.—Julius Thomsen (*Zeit. f. Physik. Chemie*).—This paper is a revision of the similar calculations of Van der Plaats. Of the two fundamental values of the atomic weights of silver and chlorine Van der Plaats deduces for the former a smaller and for the latter a considerably larger value than would follow from the author's calculations. Hence almost all the other atomic weights become too small. Whether the one or the other group of the atomic weights of these bodies (Ag, Cl, Ba, I, S, Pb, K, Na, Li, N), *i.e.*, the original values of Stas, those of the present author, and those of Van der Plaats, contains the more probable figures must doubtless appear from a comparison of the values contained on the one hand on Stas's experimental material, and on the other hand would follow if the numbers of the one or the other group of the calculated atomic weights are adopted. If we use the values of the atomic weights for chlorine and nitrogen as calculated by the author, *i.e.*, 35·4494 and 14·0396, and the proportion of the molecular weights of ammonia and hydrogen chloride, as calculated for a vacuum,—

$$\varkappa = \frac{NH_3}{HCl} = 0{\cdot}467433$$

in order to calculate the atomic weight of hydrogen according to the formula—

$$H = \frac{\varkappa Cl - N}{3 - \varkappa}$$

we find H = 0·9992; that is a value 0·0003 higher than is obtained by using the atomic weights for Cl and N as given by Stas.

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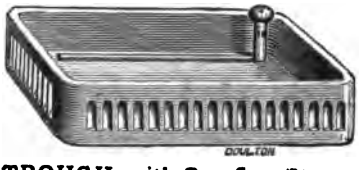

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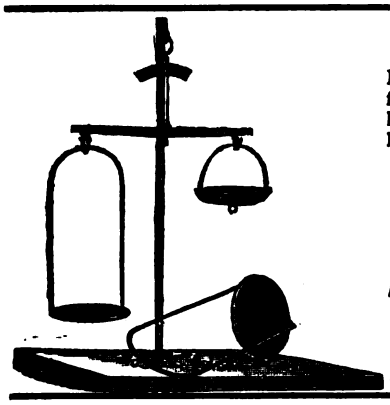

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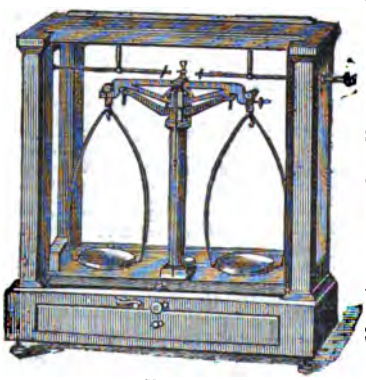

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BRITISH ASSOCIATION
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Oxford, 1894.

INAUGURAL ADDRESS OF THE PRESIDENT,

The Most Hon. The Marquis of Salisbury, K.G., D.C.L., F.R.S., Chancellor of the University of Oxford.

My functions are of a more complicated character than usually is assigned to the occupants of this Chair. As Chancellor of the University it is my duty to tender to the British Association a hearty welcome, which it is my duty as President of the Association to accept. As President of the Association I convey, most unworthily, the voice of English science, as many worthy and illustrious Presidents have done before me; but in representing the University I represent far more fittingly the learners who are longing to hear the lessons which the first teachers of English science have come as visitors to teach. I am bound to express on behalf of the University our sense of the good feeling towards that body which is the motive of this unusual arrangement. But as far as I am personally concerned, it is attended with some embarrassing results. In presence of the high priests of science I am only a layman, and all the skill of all the chemists the Association contains will not transmute a layman into any more precious kind of metal. Yet it is my hard destiny to have to address on scientific matters probably the most competent scientific audience in the world. If a country gentleman, who was also a colonel of Volunteers, were by any mental aberration on the part of the Commander-in-Chief to be appointed to review an army corps at Aldershot, all military men would doubtless feel a deep compassion for his inevitable fate. I bespeak some spark of that divine emotion when I am attempting to discharge under similar conditions a scarcely less hopeless duty. At least, however, I have the consolation of feeling that I am free from some of the anxieties which have fallen to those who have preceded me as Presidents in this city. The relations of the Association and the University are those of entire sympathy and good will, as becomes common workers in the sacred cause of diffusing enlightenment and knowledge. But we must admit that it was not always so. A curious record of a very different state of feeling came to light last year in the interesting biography of Dr. Pusey, which is the posthumous work of Canon Liddon. In it is related the first visit of the Association to Oxford in 1832. Mr. Keble, at that time a leader of University thought, writes indignantly to his friend to complain that the honorary degree of D.C.L. had been bestowed upon some of the most distinguished members of the Association: "The Oxford Doctors," he says, "have truckled sadly to the spirit of the times in receiving the hodge-podge philosophers as they did." It is amusing, at this distance of time, to note the names of the hodge-podge of philosophers whose academical distinctions so sorely vexed Mr. Keble's gentle spirit. They were Brown, Brewster, Faraday, and Dalton. When we recollect the lovable and serene character of Keble's nature, and that he was at that particular date probably the man in the University who had the greatest power over other men's minds, we can measure the distance we have traversed since that time; and the rapidity with which the converging paths of these two intellectual luminaries, the University and the Association, have approximated to each other. This sally of Mr. Keble's was no passing or accidental caprice. It represented a deep-seated sentiment in this place of learning, which had its origin in historic causes, and which has only died out in our time. One potent cause of it was that both bodies were teachers of science, but did not then in any degree attach the same meaning to that word. Science with the University for many generations bore a signification different from that which belongs to it in this assembly. It represented the knowledge which alone in the Middle Ages was thought worthy of the name of science. It was the knowledge gained not by external observation, but by mere reflection. The student's microscope was turned inward upon the recesses of his own brain; and when the supply of facts and realities failed, as it very speedily did, the scientific imagination was not wanting to furnish to successive generations an interminable series of conflicting speculations. *That* science—science in our academical sense—had its day of rapid growth, of boundless aspiration, of enthusiastic votaries. It fascinated the rising intellect of the time, and it is said—people were not particular about figures in those days—that its attractions were at one time potent enough to gather round the University thirty thousand students, who for the sake of learning its teaching were willing to endure a life of the severest hardship. Such a state of feeling is now an archæological curiosity. The revolt against Aristotle is now some three centuries old. But the mental sciences which were supposed to rest upon his writings have retained some of their ascendency even to this day, and have only slowly and jealously admitted the rivalry of the growing sciences of observation. The subject is interesting to us, as this undecided state of feeling coloured the experiences of this Association at its last Oxford visit, nearly a generation later, in 1860. The warmth of the encounters which then took place have left a vivid impression on the minds of those who are old enough to have witnessed them. That much energy was on that occasion converted into heat may, I think, be inferred from the mutual distance which the two bodies have since maintained. Whereas the visit of 1832 was succeeded by another visit in fifteen years, and the visit of 1847 was succeeded by another visit in thirteen years, the year 1860 was followed by a long and dreary interval of separation, which has only now, after four-and-thirty years, been terminated. It has required the lapse of a generation to draw the curtain of oblivion over those animated scenes. It was popularly supposed that deep divergences upon questions of religion were the motive force of those high controversies. To some extent that impression was correct. But men do not always discern the motives which are really urging them, and I suspect that in many cases religious apprehensions only masked the resentment of the older learning at the appearance and claims of its younger rival. In any case there is something worthy of note, and something that conveys encouragement, in the difference of the feeling which prevails now and the feeling that was indicated then. Few men are now influenced by the strange idea that questions of religious belief depend on the issues of physical research. Few men, whatever their creed, would now seek their geology in the books of their religion, or, on the other hand, would fancy that the laboratory or the microscope could help them to penetrate the mysteries which hang over the nature and the destiny of the soul of man. And the old learning no longer contests the share in education which is claimed by the new, or is blind to the supreme influence which natural knowledge is exercising in moulding the human mind.

A study of the addresses of my learned predecessors in this office shows me that the main duty which it falls to a President to perform in his introductory address, is to remind you of the salient points in the annals of science

since last the Association visited the town in which he is speaking. Most of them have been able to lay before you in all its interesting detail the history of the particular science of which each one of them was the eminent representative. If I were to make any such attempt I should only be telling you with very inadequate knowledge a story which is from time to time told you, as well as it can be told, by men who are competent to deal with it. It will be more suitable to my capacity if I devote the few observations I have to make to a survey not of our science but of our ignorance. We live in a small bright oasis of knowledge surrounded on all sides by a vast unexplored region of impenetrable mystery. From age to age the strenuous labour of successive generations wins a small strip from the desert and pushes forward the boundary of knowledge. Of such triumphs we are justly proud. It is a less attractive task—but yet it has its fascination as well as its uses—to turn our eyes to the undiscovered country which still remains to be won, to some of the stupendous problems of natural study which still defy our investigation. Instead, therefore, of recounting to you what has been done, or trying to forecast the discoveries of the future, I would rather draw your attention to the condition in which we stand towards three or four of the most important physical questions which it has been the effort of the last century to solve.

Of the scientific enigmas which still, at the end of the Nineteenth Century, defy solution, the nature and origin of what are called the elements is the most notable. It is not, perhaps, easy to give a precise logical reason for the feeling that the existence of our sixty-five elements is a strange anomaly and conceals some much simpler state of facts. But the conviction is irresistible. We cannot conceive, on any possible doctrine of cosmogony, how these sixty-five elements came into existence. A third of them form the substance of this planet. Another third are useful, but somewhat rare. The remaining third are curiosities scattered haphazard, but very scantily, over the globe, with no other apparent function but to provide occupation for the collector and the chemist. Some of them are so like each other that only a chemist can tell them apart; others differ immeasurably from each other in every conceivable particular. In cohesion, in weight, in conductivity, in melting-point, in chemical proclivities they vary in every degree. They seem to have as much relation to each other as the pebbles on a sea-beach, or the contents of an ancient lumber-room. Whether you believe that Creation was the work of design or of inconscient law, it is equally difficult to imagine how this random collection of dissimilar materials came together. Many have been the attempts to solve this enigma; but up till now they have left it more impenetrable than before. A conviction that here was something to discover lay beneath the persistent belief in the possibility of the transmutation of other metals into gold, which brought the alchemy of the Middle Ages into being. When the immortal discovery of Dalton established that the atoms of each of these elements have a special weight of their own, and that consequently they combine in fixed ponderable proportions from which they never depart, it renewed the hope that some common origin of the elements was in sight. The theory was advanced that all these weights were multiples of the weight of hydrogen—in other words, that each elementary atom was only a greater or a smaller number of hydrogen atoms compacted by some strange machinery into one. The most elaborate analyses, conducted by chemists of the highest eminence —conspicuously by the illustrious Stas—were directed to the question whether there was any trace in fact of the theoretic idea that the atoms of each element consist of so many atoms or even of so many half-atoms of hydrogen. But the reply of the laboratories has always been clear and certain—that there is not in the facts the faintest foundation for such a theory.

Then came the discovery of the spectral analysis, and men thought that with an instrument of such inconceivable delicacy we should at last find out something as to the nature of the atom. The result has been wholly disappointing. Spectral analysis in the hands of Dr. Huggins and Mr. Lockyer and others has taught us things of which the world little expected to be told. We have been enabled to measure the speed with which clouds of blazing hydrogen course across the surface of the sun: we have learnt the pace—the fabulous pace—at which the most familar stars have been for ages approaching to or receding from our planet, without apparently affecting the proportions of the patterns which as far as historical record goes back they have always delineated on the evening sky. We have received some information about the elementary atoms themselves. We have learnt that each sort of atom when heated strikes upon the ether a vibration, or set of vibrations, whose rate is all its own; and that no one atom or combination of atoms in producing its own spectrum encroaches even to the extent of a single line upon the spectrum that is peculiar to its neighbour. We have learnt that the elements which exist in the stars and specially in the sun, are mainly those with which we are familiar upon earth. There are a few lines in excess to which we can give no terrestrial name; and there are some still more puzzling gaps in our list. It is a great aggravation of the mystery which besets the question of the elements, that among the lines which are absent from the spectrum of the sun, those of nitrogen and oxygen stand first. Oxygen constitutes the largest portion of the solid and liquid substance of our planet, so far as we know it; and nitrogen is very far the predominent constituent of our atmosphere. If the earth is a detached bit whirled off the mass of the sun, as cosmogonists love to tell us, how comes it that in leaving the sun we cleaned him out so completely of his nitrogen and oxygen that not a trace of these gases remained behind to be discovered even by the sensitive vision of the spectroscope.

All these things the discovery of spectrum analysis has added to our knowledge; but it has left us as ignorant as ever as to the nature of the capricious differences which separate the atoms from each other, or the cause to which those differences are due.

In the last few years the same enigma has been approached from another point of view by Professor Mendeleeff. The periodic law which he has discovered reflects on him all the honour that can be earned by ingenious, laborious, and successful research. He has shown that this perplexing list of elements can be divided into families of about seven, speaking very roughly; that those families all resemble each other in this, that as to weight, volume, heat, and laws of combination, the members of each family are ranked among themselves in obedience to the same rule. Each family differs from the others; but each internally is constructed upon the same plan. It was a strange discovery—strangest of all in its manifest defects. For in the plan of his families there were blanks left; places not filled up because the properly constituted elements required according to his theory had not been found to fill them. For the moment their absence seemed a weakness in the Professor's idea, and gave an arbitrary aspect to his scheme. But the weakness was turned into strength when, to the astonishment of the scientific world, three of the elements which were missing made their appearance in answer to his call. He had described beforehand the qualities they ought to have; and gallium, germanium, and scandium, when they were discovered shortly after the publication of his theory, were found to be duly clothed with the qualities he required in each. This remarkable confirmation has left Mendeleeff's periodic law in an unassailable position. But it has rather thickened than dissipated the mystery which hangs over the elements. The discovery of these co-ordinate families dimly points to some identical origin, without suggesting the method of their genesis or the nature of their common parentage. If they were organic beings all our difficulties would be solved by muttering the comfort-

able word "evolution"—one of those indefinite words from time to time vouchsafed to humanity, which have the gift of alleviating so many perplexities and masking so many gaps in our knowledge. But the families of elementary atoms do not breed; and we cannot therefore ascribe their ordered difference to accidental variations perpetuated by heredity under the influence of natural selection. The rarity of iodine, and the abundance of its sister chlorine, cannot be attributed to the survival of the fittest in the struggle for existence. We cannot account for the minute difference which persistently distinguishes nickel from cobalt, by ascribing it to the recent inheritance by one of them of an advantageous variation from the parent stock.

The upshot is that all these successive triumphs of research, Dalton's, Kirchhoff's, Mendeleeff's, greatly as they have added to our store of knowledge, have gone but little way to solve the problem which the elementary atoms have for centuries presented to mankind. What the atom of each element is, whether it is a movement, or a thing, or a vortex, or a point having inertia, whether there is any limit to its divisibility, and, if so, how that limit is imposed, whether the long list of elements is final, or whether any of them have any common origin, all these questions remain surrounded by a darkness as profound as ever. The dream which lured the alchemists to their tedious labours, and which may be said to have called chemistry into being, has assuredly not been realised, but it has not yet been refuted. The boundary of our knowledge in this direction remains where it was many centuries ago.

The next discussion to which I should look in order to find unsolved riddles which have hitherto defied the scrutiny of science, would be the question of what is called the ether. The ether occupies a highly anomalous position in the world of science. It may be described as a half-discovered entity. I dare not use any less pedantic word than entity to designate it, for it would be a great exaggeration of our knowledge if I were to speak of it as a body or even as a substance. When nearly a century ago, Young and Fresnel discovered that the motions of an incandescent particle were conveyed to our eyes by undulation, it followed that between our eyes and the particle there must be something to undulate. In order to furnish that something, the notion of the ether was conceived, and for more than two generations the main, if not the only, function of the word ether has been to furnish a nominative case to the verb "to undulate." Lately, our conception of this entity has received a notable extension. One of the most brilliant of the services which Professor Maxwell has rendered to science has been the discovery that the figure which expressed the velocity of light, also expressed the multiplier required to change the measure of static or passive electricity into that of dynamic or active electricity. The interpretation reasonably affixed to this discovery is that, as light and the electric impulse move approximately at the same rate through space, it is probable that the undulations which convey them are undulations of the same medium. And as induced electricity penetrates through everything, or nearly everything, it follows that the ether through which its undulations are propagated must pervade all space, whether empty or full, whether occupied by opaque matter or transparent matter, or by no matter at all. The attractive experiments by which the late Professor Herz illustrated the electric vibrations of the ether will only be alluded to by me, in order that I may express the regret deeply and generally felt that death should have terminated prematurely the scientific career which had begun with such brilliant promise and such fruitful achievements. But the mystery of the ether, though it has been made more fascinating by these discoveries, remains even more inscrutable than before. Of this all-pervading entity we know absolutely nothing except this one fact, that it can be made to undulate. Whether outside the influence of matter on the motion of its waves, ether has any effect on matter or matter upon it, is absolutely unknown. And even its solitary function of undulating ether performs in an abnormal fashion which has caused infinite perplexity. All fluids that we know transmit any blow they have received by waves which undulate backwards and forwards in the path of their own advance. The ether undulates athwart the path of the wave's advance. The genius of Lord Kelvin has recently discovered what he terms a labile state of equilibrium, in which a fluid that is infinite in its extent may exist, and may undulate in this eccentric fashion without outraging the laws of mathematics. I am no mathematician, and I cannot judge whether this reconciliation of the action of the ether with mechanical law is to be looked upon as a permanent solution of the question, or is only what diplomatists call a *modus vivendi*. In any case it leaves our knowledge of the ether in a very rudimentary condition. It has no known qualities except one, and that quality is in the highest degree anomalous and inscrutable. The extended conception which enables us to recognise ethereal waves in the vibrations of electricity has added infinite attraction to the study of those waves, but it carries its own difficulties with it. It is not easy to fit in the theory of electrical ether waves with the phenomena of positive and negative electricity, and as to the true significance and cause of those counteracting and complementary forces, to which we give the provisional names of negative and positive, we know about as much now as Franklin knew a century and a half ago.

I have selected the elementary atoms and the ether as two instances of the obscurity that still hangs over problems which the highest scientific intellects have been investigating for several generations. A more striking but more obvious instance still is Life—animal and vegetable Life—the action of an unknown force on ordinary matter. What is the mysterious impulse which is able to strike across the ordinary laws of matter, and twist them for a moment from their path? Some people demur to the use of the term "vital force" to designate this impulse. In their view the existence of such a force is negatived by the fact that chemists have been able by cunning substitutions to produce artificially the peculiar compounds which in nature are only found in organisms that are or have been living. These compounds are produced by some living organism in the performance of the ordered series of functions proper to its brief career. To counterfeit them—as has been done in numerous cases—does not enable us to do what the vital force alone can effect—to bring the organism itself into existence, and to cause it to run its appointed course of change. This is the unknown force which continues to defy not only our imitation but our scrutiny. Biology has been exceptionally active and successful during the last half-century. Its triumphs have been brilliant, and they have been rich enough not only in immediate result but in the promise of future advance. Yet they give at present no hope of penetrating the great central mystery. The progress which has been made in the study of microscopic life has been very striking, whether or not the results which are at present inferred from it can be taken as conclusive. Infinitesimal bodies found upon the roots of plants have the proud office of capturing and taming for us the free nitrogen of the air, which, if we are to live at all, we must consume and assimilate, and yet which, without the help of our microscopic ally, we could not draw for any useful purpose from the ocean of nitrogen in which we live. Microscopic bodies are convicted of causing many of the worst diseases to which flesh is heir, and the guilt of many more will probably be brought home to them in due time; and they exercise a scarcely less sinister or less potent influence on our race by the plagues with which they destroy some of the most valuable fruits of husbandry, such as the potato, the mulberry, and the vine. Almost all their power resides in the capacity of propagating their kind with infinite rapidity, and up to this time science has been more skilful in describing their

ravages than in devising means to hinder them. It would be ungrateful not to mention two brilliant exceptions to this criticism. The antiseptic surgery which we owe chiefly to Lister; and the inoculation against anthrax, hydrophobia, and perhaps some other diseases, which we owe to Pasteur, must be recorded as splendid victories over the countless legions of our infinitesimal foes. Results like these are the great glory of the scientific workers of the past century. Men may, perhaps, have overrated the progress of nineteenth-century research in opening the secrets of nature; but it is difficult to overrate the brilliant service it has rendered in ministering to the comforts and diminishing the sufferings of mankind.

If we are not able to see far into the causes and origin of life in our own day, it is not probable that we shall deal more successfully with the problem as it arose many million years ago. Yet certainly the most conspicuous event in the scientific annals of the last half-century has been the publication of Mr. Darwin's work on the "Origin of Species," which appeared in 1859. In some respects, in the depth of the impression which it made on scientific thought, and even on the general opinion of the world, its momentous effect can hardly be overstated. But at this distance of time it is possible to see that some of its success has been due to adventitious circumstances. It has had the chance of enlisting among its champions some of the most powerful intellects of our time, and perhaps the still happier fortune of appearing at a moment when it furnished an armoury of weapons to men, who were not scientific, for use in the bitter but transitory polemics of the day. But far the largest part of its accidental advantages was to be found in the remarkable character and qualifications of its author. The equity of judgment, the simple-minded love of truth, and the patient devotion to the pursuit of it through years of toil and of other conditions the most unpropitious—these things endeared to numbers of men everything that came from Charles Darwin apart from its scientific merit or literary charm. And whatever final value may be assigned to his doctrine, nothing can ever detract from the lustre shed upon it by the wealth of his knowledge and the infinite ingenuity of his resource. The intrinsic power of his theory is shown at least in this one respect, that in the department of knowledge with which it is concerned it has effected an entire revolution in the methods of research. Before his time the study of living nature had a tendency to be merely statistical; since his time it has become predominantly historical. The consideration how any organic body came to be what it is occupies a far larger area in any inquiry now than the mere description of its actual condition; but this question was not predominant—it may almost be said to have been ignored—in the Botanical and Zoological study of sixty years ago.

Another lasting and unquestioned effect has resulted from Darwin's work. He has, as a matter of fact, disposed of the doctrine of the immutability of species. It has been mainly associated in recent days with the honoured name of Agassiz, but with him has disappeared the last defender of it who could claim the attention of the world. Few now are found to doubt that animals separated by differences far exceeding those that distinguish what we know as species have yet descended from common ancestors. But there is much less agreement as to the extent to which this common descent can be assumed, or the process by which it has come about. Darwin himself believed that all animals were descended from "at most four or five progenitors"—adding that "there was grandeur in the view that life had been originally breathed by the Creator into a few forms or one." Some of his more devoted followers, like Professor Haeckel, were prepared to go a step farther and to contemplate a crystal as the probable ancestor of the whole fauna and flora of this planet.

To this extent the Darwinian theory has not effected the conquest of scientific opinion; and still less is there any unanimity in the acceptance of natural selection as the sole or even the main agent of whatever modifications may have led up to the existing forms of life. The deepest obscurity still hangs over the origin of the infinite variety of life. Two of the strongest objections to the Darwinian explanation appear still to retain all their force.

I think Lord Kelvin was the first to point out that the amount of time required by the advocates of the theory for working out the process they had imagined could not be conceded without assuming the existence of a totally different set of natural laws from those with which we are acquainted. His view was not only based on profound mechanical reasoning, but it was so plain that any layman could comprehend it. Setting aside arguments deduced from the resistance of the tides, which may be taken to transcend the lay understanding, his argument from the refrigeration of the earth requires little science to apprehend it. Everybody knows that hot things cool, and that according to their substance they take more or less time in cooling. It is evident from the increase of heat as we descend into the earth that the earth is cooling, and we know by experiment, within certain wide limits, the rate at which its substances, the matters of which it is constituted, are found to cool. It follows that we can approximately calculate how hot it was so many million years ago. But if at any time it was hotter at the surface by 50° F. than it is now, life would then have been impossible upon the planet, and therefore we can without much difficulty fix a date before which organic life on earth cannot have existed. Basing himself on these considerations, Lord Kelvin limited the period of organic life upon the earth to a hundred million years, and Professor Tait in a still more penurious spirit cut that hundred down to ten. But on the other side of the account stand the claims of the geologists and biologists. They have revelled in the prodigality of the ciphers which they put at the end of the earth's hypothetical life. Long cribbed and cabined within the narrow bounds of the popular chronology, they have exulted wantonly in their new freedom. They have lavished their millions of years with the open hand of a prodigal heir indemnifying himself by present extravagance for the enforced self-denial of his youth. But it cannot be gainsaid that their theories require at least all this elbowroom. If we think of that vast distance over which Darwin conducts us from the jelly-fish lying on the primeval beach to man as we know him now; if we reflect that the prodigious change requisite to transform one into the other is made up of a chain of generations, each advancing by a minute variation from the form of its predecessor, and if we further reflect that these successive changes are so minute that in the course of our historical period—say three thousand years—this progressive variation has not advanced by a single step perceptible to our eyes in respect to man or the animals and plants with which man is familiar, we shall admit that for a chain of change so vast, of which the smallest link is longer than our recorded history, the biologists are making no extravagant claim when they demand at least many hundred million years for the accomplishment of the stupendous process. Of course, if the mathematicians are right, the biologists cannot have what they demand. If, for the purposes of their theory, organic life must have existed on the globe more than a hundred million years ago, it must, under the temperature then prevailing, have existed in a state of vapour. The jelly-fish would have been dissipated in steam long before he had had a chance of displaying the advantageous variation which was to make him the ancestor of the human race. I see, in the eloquent discourse of one of my most recent and most distinguished predecessors in this chair, Sir Archibald Geikie, that the controversy is still alive. The mathematicians sturdily adhere to their figures, and the biologists are quite sure the mathematicians must have made a mistake. I will not get myself into the line of fire by intervening in such a controversy. But until it is adjusted the laity may be excused for re-

turning a verdict of "not proven" upon the wider issues the Darwinian school has raised.

The other objection is best stated in the words of an illustrious disciple of Darwin, who has recently honoured this city by his presence—I refer to Professor Weismann. But in referring to him I cannot but give, in passing, a feeble expression to the universal sorrow with which in this place the news was received that Weismann's distinguished antagonist, Professor Romanes, had been taken from us in the outset and full promise of a splendid scientific career.

The gravest objection to the doctrine of natural selection was expressed by Weismann in a paper published a few months ago, not as agreeing to the objection, but as resisting it; and therefore his language may be taken as an impartial statement of the difficulty. "We accept natural selection," he says, "not because we are able to demonstrate the process in detail, not even because we can with more or less ease imagine it, but simply because we must—because it is the only possible explanation that we can conceive. We must assume natural selection to be the principle of the explanation of the metamorphoses, because all other apparent principles of explanation fail us, and it is inconceivable that there could yet be another capable of explaining the adaptation of organisms without assuming the help of a principle of design."

There is the difficulty. We cannot demonstrate the process of natural selection in detail; we cannot even, with more or less ease, imagine it. It is purely hypothetical. No man, so far as we know, has ever seen it at work. An accidental variation may have been perpetuated by inheritance, and in the struggle for existence the bearer of it may have replaced, by virtue of the survival of the fittest, his less improved competitors; but as far as we know no man or succession of men have ever observed the whole process in any single case, and certainly no man has recorded the observation. Variation by *artificial* selection, of course, we know very well; but the intervention of the cattle breeder and the pigeon fancier is the essence of artificial selection. It is effected by their action in crossing, by their skill in bringing the right mates together to produce the progeniture they want. But in natural selection who is to supply the breeder's place? Unless the crossing is properly arranged, the new breed will never come into being. What is to secure that the two individuals of opposite sexes in the primeval forest who have been both accidentally blessed with the same advantageous variation shall meet and transmit by inheritance that variation to their successors? Unless this step is made good, the modification will never get a start: and yet there is nothing to insure that step, except pure chance. The law of chances takes the place of the cattle breeder and the pigeon fancier. The biologists do well to ask for an immeasurable expanse of time, if the occasional meetings of advantageously varied couples from age to age are to provide the pedigree of modifications which unite us to our ancestor the jelly-fish. Of course the struggle for existence, and the survival of the fittest, would in the long run secure the predominance of the stronger breed over the weaker. But it would be of no use in setting the improved breed going. There would not be time. No possible variation which is known to our experience, in the short time that elapses in a single life between the moment of maturity and the age of reproduction, could enable the varied individual to clear the field of all competitors, either by slaughtering or starving them out. But unless the struggle for existence took this summary and internecine character, there would be nothing but mere chance to secure that the advantageously varied bridegroom at one end of the wood should meet the bride, who by a happy contingency had been advantageously varied in the same direction at the same time at the other end of the wood. It would be a mere chance if they ever knew of each other's existence—a still more unlikely chance that they should resist on both sides all temptations to a less advantageous alliance. But unless they did so, the new breed would never even begin, let alone the question of its perpetuation after it had begun. I think Professor Weismann is justified in saying that we cannot, either with more or less ease, imagine the process of natural selection.

It seems strange that a philosopher of Professor Weismann's penetration should accept as established a hypothetical process, the truth of which he admits that he cannot demonstrate in detail, and the operation of which he cannot even imagine. The reason that he gives seems to me instructive of the great danger scientific research is running at the present time—the acceptance of mere conjecture in the name and place of knowledge, in preference to making frankly the admission that no certain knowledge can be attained. "We accept natural selection," he says, "because we must—because it is the only possible explanation that we can conceive." As a politician I know that argument very well. In political controversy it is sometimes said of a disputed proposal that it "holds the field," that it must be accepted because no possible alternative has been suggested. In politics there is occasionally a certain validity in the argument, for it sometimes happens that some definite course must be taken, even though no course is free from objection. But such a line of reasoning is utterly out of place in science. We are under no obligation to find a theory if the facts will not provide a sound one. To the riddles which nature propounds to us the profession of ignorance must constantly be our only reasonable answer. The cloud of imprenetrable mystery hangs over the development and still more over the origin of life. If we strain our eyes to pierce it, with the foregone conclusion that some solution is and must be attainable, we shall only mistake for discoveries the figments of our own imagination. Professor Weismann adds another reason for his belief in natural selection which is certainly characteristic of the time in which we live. "It is inconceivable," he says, "that there should be another principle capable of explaining the adaptation of organisms without assuming the help of a principle of design." The whirligig of time assuredly brings its revenges. Time was, not very long ago, when the belief in creative design was supreme. Even those who were sapping its authority were wont to pay it a formal homage, fearing to shock the public conscience by denying it. Now the revolution is so complete that a great philosopher uses it as a *reductio ad absurdum*, and prefers to believe that which can neither be demonstrated in detail nor imagined, rather than run the slightest risk of such a heresy.

I quite accept the Professor's dictum that if natural selection is rejected we have no resource but to fall back on the mediate or immediate agency of a principle of design. In Oxford, at least, he will not find that argument is conclusive, nor, I believe, among scientific men in this country generally, however imposing the names of some whom he may claim for that belief. I would rather lean to the conviction that the multiplying difficulties of the mechanical theory are weakening the influence it once had acquired. I prefer to shelter myself in this matter behind the judgment of the greatest living master of natural science among us, Lord Kelvin, and to quote as my own concluding words the striking language with which he closed his address from this chair more than twenty years ago: "I have always felt," he said, "that the hypothesis of natural selection does not contain the true theory of evolution, if evolution there has been in biology. . . . I feel profoundly convinced that the argument of design has been greatly too much lost sight of in recent zoological speculations. Overpoweringly strong proofs of intelligent and benevolent design lie around us, and if ever perplexities, whether metaphysical or scientific, turn us away from them for a time, they come back upon us with irresistible force, showing to us through nature the influence of a free will, and teaching us that all living things depend on one everlasting Creator and Ruler."

THE SEPARATION OF THE RARE EARTHS.*

By HENRY A. ROWLAND.

In the course of several years' investigations of the so-called "rare earths," such as yttrium, erbium, holmium, cerium, &c., I have devised several methods for their separation. I wish to give an account of these now, and hope soon to be able to publish a complete description of my work and its results.

It was evident very early in the work that cerium, lanthanum, praseodymium, neodymium, and thorium differed from the yttrium group, and I have seen no reason to suppose that they can be divided any further. All of these "earths" appear in varying proportions in such minerals as gadolinite, samarskite, yttrialite, cerite, &c. Besides the elements of the cerium group here present, there are at least seven other substances. For the present I shall speak of them as—

a, *b*, *i*, *d*, *h*, *n*, *c*, *k*.

Their properties are as follows:—

Properties of Elements.

Substance a.

This is the principal element of yttrium, and may possibly be divided into two in the future, as I have observed a variation in the arc spectrum on adding potash or soda. However, this is no more evidence than occurs in the case of iron or zirconium. I give a process below for producing this pure.

Properties.—No absorption bands. Oxalate and oxide pure white. It occurs in the sun. Its properties are those of yttrium as hitherto obtained, but I am the first to obtain it with any approach to purity.

Mixture of b, i, and d.

These seem to be the principal ingredients in so-called "erbium."

Oxalate is red. Oxide is pure white. Absorption band is that of "erbium." It colours the electric arc green, and shows the "erbium" emission bands on heating white hot. The substance *b* is strong in gadolinite and weak in samarskite. The solution has the absorption bands of "erbium," and most of these seem to belong to *b* rather than *i*. However, we can readily prove that the absorption bands of erbium belong to two substances, as we can produce a decided variation in it.

I cannot reconcile this with my spectrum work without assuming a *fourth* ingredient in "erbium."

Substance *b* is in the sun, but not *i*. With *b* and *i* the substance *d* always occurs.

Substance d.

This is the principal impurity of a sample of yttrium, kindly furnished me by Dr. Krüss, which my process of making yttrium separates out. It has not been obtained pure, but occurs strongly in the yellow part of the oxides. It is in the sun.

By aid of ferrocyanide of potassium the substance *a* can be obtained pure from *d*. With this exception *d* occurs in all preparations of the yttrium group, and cannot be separated from *b*, *i*, *c*, *n*, *h*, or any of the other substances. Indeed, I have found it in some specimens of cerium and lanthanum, although in traces only.

On account of the trouble caused by it and its universal presence, I propose the name demonium for it.

Its principal spectrum line is at wave-length 4000·6 nearly.

Substance h.

This occurs mainly in samarskite. Hints toward its separation will be given below, but I have otherwise obtained none of its properties.

* From the *Johns Hopkins University Circular*, May, 1894.

Substances n, k, and c.

These always occur with *d*, and form a group intermediate between the yttrium and cerium groups. They can be separated from these by sulphate of potassium or sodium by always taking in intermediate portions of the precipitate. They seem to have a weak absorption-spectrum in the visible spectrum, and strong in the ultra-violet, especially *k*.

Chemical Separation.

The first process that suggests itself is that by the sulphates of soda or potash. This is the usual method for separating the cerium from the yttrium groups. When the solution of earth and the sulphate solution are both hot and concentrated, everything except some scandium comes down. When done in the cold with weaker solutions, there is more or less complete separation of the cerium group. Let the mixed earths be dissolved in a very slight excess of nitric acid and diluted somewhat (possibly 1 kilo. to 2 or 3 litres). Place in a warm place, add lumps of sulphate of soda, and stir until no more will dissolve. Continue to add and stir for a day or two until the absorption lines of neodymium disappear from the solution. Filter off and call the solution No. 1. Add caustic potash to the precipitated sulphates and wash so as to leave the oxides once more. Dissolve in nitric acid and precipitate again with sulphate of soda, calling the filtrate No. 2. Proceed in this way possibly ten or more times. The filtrates contain less and less earths, and the precipitate is more and more the pure cerium group; but a dozen precipitations still leave some impurity.

The portions 1, 2, 3, &c., show decreasing "erbium" absorption bands, and the spectrum shows that the substances *a*, *b*, *d*, *i* are gradually separated out with parts 1, 2, &c., while the numerous fine lines belonging to *d*, *n*, *c*, &c., with the cerium group fill the spectrum of the portions 8, 9, 10, &c. This intermediate group has only very weak absorption bands, and evidently has three or four elements in it, as I have produced at least that number of variations in its spectrum. The group can be obtained fairly free from *a*, *b*, and *i*, but the substance *d* persists in all the filtrates and in the precipitated cerium group also. This intermediate group *d*, *n*, &c., seems to be in greater proportion in samarskite than gadolinite, and there seem to be more elements in samarskite than in gadolinite. One of these I have called *h*.

The oxides, especially for samarskite, are very yellow and dark.

Sulphate of potash has a decided action in separating *a* and *i* from *b*, *a* and *i* coming down first. After two months, the solution gradually drying, the proportion of *b* to *a* in the filtrate increased many times. Sulphate of soda has an action of the same kind, but much weaker. After leaving two months over sulphate of potash and soda, the following was the result of analysis of the soluble part as compared with the original mixture:—

	Sulphate of potash.	Sulphate of soda.
Ce, La, &c.	0	0
a	Weak	Medium weak
b	Much stronger	Stronger
c	0	0
d	Unchanged	Unchanged
i	Weaker	Medium strong
o	Stronger	Weaker

The oxide of the members of this group which are only slightly precipitated by the sulphates of soda and potash is pure snow-white, and hence those of *b* and *i* must be so.

The substance *d* comes down slightly sooner than *a* by sulphate of soda, but slightly slower by sulphate of potash. Hence in purifying yttrium (substance *a*) for the last time from the Ce group, sulphate of potash will increase *d* in the filtrate, and sulphate of soda will decrease it.

Action of Oxalic Acid.

When the oxalates of the mixed earths, free from the Ce group, are boiled in water to which nitric acid is added, they are more or less dissolved, leaving a coarse heavy red oxalate yielding a pale yellow oxide. The filtrate, set aside to cool, deposits more of the oxalates and leaves a filtrate which contains several of the unknown elements, as also what remains of the Ce group. On separating the Ce group the remainder is quite different from the heavy red oxalate, but there is far from complete separation. The analysis showed the following:—

a, b, c, d, h, i, n.

I have not found the separation particularly useful, and it seems to be more apparent than real as tested by the spectroscope.

Ferrocyanide of Potassium.

This is the most useful process, and easily separates the element *a* pure and free from all others. To obtain pure *a* from the mineral gadolinite, *Fergusonite, or Samarskite:*

First obtain the crude-mixed earths in the usual manner; then separate the cerium group as usual until the absorption bands of neodymium no longer appear. For the complete separation without loss this must be done several times, as much of the yttrium group is carried down with the first precipitate, as we have before seen.

The separation of the yttrium (*a*) from the other elements is effected by precipitating the latter from a weak acid solution by ferrocyanide of potassium. For this purpose the filtrate, after separating the cerium group, can be used at once by slightly acidulating with nitric acid, diluting, and adding a weak solution of ferrocyanide of potassium. No precipitate should appear at once, but by standing for an hour or so some will come down. Add more ferrocyanide of potassium, and repeat until the filtrate no longer shows the bands of so-called erbium. After this it is best to precipitate with oxalic acid or oxalate of potassium, and ignite the precipitate so as to get the earth. Dissolve this in nitric acid, and add only water enough to make a very concentrated syrupy solution. Place in a beaker at least three inches in diameter, and examine with a spectroscope of low power for absorption bands. Probably the bands of neodymium and "erbium" will appear. Separate the first by sulphate of sodium as usual, and the last by ferrocyanide of potassium from an acid solution as above. The filtrate will then contain the pure yttrium *a*, whose calcined oxalate will be pure white without trace of yellow. After separation of iron, calcium, and possibly manganese, the earth will be a pure element as far as I can tell spectroscopically. However, like Zr, Fe, and many other substances, the addition of Na or K to the electric arc while obtaining the spectrum will change the intensity of certain lines of the spectrum, while others are unchanged. If this is considered as evidence of the existence of two elements, then the same evidence will apply to Fe and Zr. The reason for believing that the substance thus found is an element is based on the fact that its spectrum remains unaltered in all minerals and after all chemical operations that I have been able to devise. Furthermore, I believe that the new process is not only more easy than any other, but also that it has given a single element for the first time, as it eliminates the element *d*. The yield will of course depend on the amount of purity required. From the earths of gadolinite about one-tenth of quite pure yttrium *a* can be obtained, and about one-twentieth of very pure.

I have determined spectroscopically that when, by the above process, the absorption band of "erbium" at last disappears from 3 inches of strong solution, all the other elements have also disappeared.

By taking the first precipitate several times by ferrocyanide of potassium from an acid solution, a mixture of many elements is obtained which contains much of that element to which the so-called "erbium" band is due. By dissolving a weighed quantity of this mixture in nitric acid and water and examining the band spectrum, I have determined the limit when the band can no longer be seen. Thus I have proved that when the band vanishes from 3 inches of concentrated syrupy solution of yttrium there cannot exist in it more than ½ per cent of the mixed element as compared with the yttrium, and there is probably less.

I have not found ferrocyanide of potassium useful in the further separation or the elements, but only in separating out *a* from the others.

When the neodymium band has disappeared by use of sulphate of sodium, all the other elements of the cerium group have disappeared. The element thorium is sometimes present in the crude earths, but disappears after a while from the purified earths. The conditions for its disappearance I have not determined.

The elements which persist to the last by the ferrocyanide process are *b* and *i*, while by Krüss's process the element *d* persists the longest. As *b*+*i* has an absorption-spectrum and *d* probably not, the test of purity by absorption bands is very complete in the new process.

Note.—For help in this investigation my thanks are due to a large number of gentlemen. Professor Schapleigh has sent me a large collection of substances, Mr. Hidden, Professor Wolcott Gibbs, and Professor F. W. Clark many minerals, Professor Krüss several specimens, and Professor Barker and others have helped me in many ways.

ON THE DISCOVERY OF A NEW CLASS OF IODIFEROUS, NON-NITROGENOUS ORGANIC BASES.

By CHRISTOPHER HARTMANN and VICTOR MEYER.

In connection with the paper inserted in the last issue of the Chemical News (vol. lxx., p. 52) on some of the properties of the Iodonium Bases we give an account of their discovery (*Berichte*, vol. xxvii., p. 426).

The noteworthy fact that iodosobenzoic acid has almost entirely lost the acid character of iodobenzoic acid and nearly assumed the character of a phenol indicates that the group I : O possesses not the acid character which might be expected, but rather basic properties. In fact, iodosobenzol free from carboxyl, $C_6H_5.IO$, possesses in so far a basic character that, according to the observation of Willgerodt, it forms with acids well-characterised salts. These discoveries, surprising as they appear, render it probable that the hypothetical compound H.I : O should not be named "hypoiodous acid," but must rather be a base. Hence we attempted to saponify iodosobenzene by ebullition with dilute sulphuric acid in order to split it up into phenol and a salt of the supposed base. Dilute sulphuric acid dissolves iodosobenzol with formation of a salt, but, on boiling, its reaction did not appear distinctly modified. If the solution is now evaporated down and heated for a considerable time on the water-bath it loses the power of separating iodine from an acid solution of potassium iodide and contains an inactive base of totally modified properties. It is obtained quickly and smoothly as follows:—

It has not hitherto been found practicable to produce the free base in the anhydrous state, but the preparation of its salts presents no difficulty. We introduce 5 grms. iodosobenzene in small portions into about 75 grms. of refrigerated concentrated sulphuric acid. The solution takes a dirty brown colour and contains not a trace of iodosobenzene sulphate, for it no longer separates iodine from solution of potassium iodide, and is a solution of the

sulphate of the new base. It is refrigerated with ice and diluted with fragments of ice, whereby if we proceed cautiously there ensues only a slight turbidity, which, judging from the odour, proceeds from liberated benzene iodides. If the dilute sulphuric solution is set aside for about two days the small quantities of resin attach themselves firmly to the sides of the glass and the clear liquid can be decanted off. Or the liquid is filtered and used, preparing the haloid salts of the base. Thus we obtain from 1 part iodosobenzene 1 part of the hydriodate of the base, *i.e.*, 82·7 per cent of the theoretical quantity shown in the equation to be subsequently given.

Iodobenzene, if similarly treated, yields the same iodide, but in decidedly smaller quantity.

The transposition ensues apparently in a similar manner with para-iodoso toluene. Hence the reaction is apparently general.

The salts of the base resemble those of lead and silver, but still more those of thallium. The sulphate is readily soluble, the nitrate less so; the iodide is an insoluble yellow precipitate; the bromide is a very faintly yellow and the chloride a white precipitate, both rather more soluble than the iodide. Potassium chromate gives a fiery yellow precipitate of the chromate.

The determination of the hydrocarbons can, on account of the high percentage of iodine and its sparing combustibility, be effected only by the use of a mixture of lead chromate and potassium dichromate, with the interposition of a long stratum of silver.

The hydrogen was determined by the method of V. Meyer and Treadwell as H = 1·68 per cent. Hence the substance has the formula $C_{12}H_9I_3$.

To verify this formula it was submitted to dry distillation, when it was resolved into mono- and di-iodobenzene according to the equation $C_{12}H_9I_3 = C_6H_5I + C_6H_4I_2$. The decomposition was traced qualitatively and quantitatively in order to prove whether any by-products appeared.

We first ascertained by undertaking the decomposition in a closed space that no gases were liberated. The products of the decomposition were taken up with ether, shaken up with sulphurous acid to remove any iodine, the ether evaporated off, and the residue distilled. At 170°—190° an oil passed over (iodobenzene boils at 188°), which yielded with nitric acid a nitro-derivative melting at 172° (paraiodonitrobenzene melts at 171·5°); at 270° to 290° a substance which congeals in the receiver (paradiiodobenzene boils at 285°), and which when crystallised from ligroin melted at 129°, thus proving to be paradiiodobenzene (melting-point 129·4°).

In addition to the iodobenzenes there appeared only a minimum carbonaceous residue and iodine in insignificant quantity. If this substance had a formula including two more atoms of hydrogen, there would appear on distillation, in addition to the above-named products, hydrogen or hydrogen iodide along with benzene or a larger proportion of benzene monoiodide than was actually obtained. If it contained two atoms of hydrogen less, a smooth scission into benzene mono- and di-iodide would be impossible.

The free base must have the composition $C_{12}H_9I_2OH$.

Its formation from iodosobenzene and concentrated sulphuric acid permits us to infer its constitution. If we consider that the action of the sulphuric acid first occasions the apposition of water to the iodosobenzene, and that this addition product then reacts with a second mol. of iodosobenzene, water and oxygen being split off, we have for the free base the formula—

$$\begin{matrix} C_6H_5 \\ IC_6H_4 \end{matrix}\!\!>\!I.OH$$

according to the equations—

$$1.\ C_6H_5IO + H_2O = C_6H_2O = C_6H_5I\!<\!\begin{matrix} OH \\ OH \end{matrix}$$

$$2.\ C_6H_5I\!<\!\begin{matrix} OH \\ \boxed{OH+H} \end{matrix} C_6H_4IO =$$

$$= \begin{matrix} C_6H_5 \\ IC_6H_4 \end{matrix}\!\!>\!IOH + H_2O + O.$$

Free oxygen does not escape in the reaction.

If we accept the above constitutional formula the new base appears as a derivative of a hypothetical iodine-base analogous to hydroxylamine in its composition :—

$$N\!<\!\begin{matrix} H \\ H \\ OH \end{matrix} \qquad I\!<\!\begin{matrix} H \\ H \\ OH \end{matrix}$$

Our base, however, is analogous to hydroxylamine only in its formulæ, but not in its chemical behaviour. Hydroxylamine is an amine base which forms salts by the direct addition of the acid molecule. But the new bases behave like ammonium bases and combine with acids, the hydroxyl of the base being eliminated with a separation of water.

We have recently obtained the simplest member of the new series, the base—

$$I\!<\!\begin{matrix} C_6H_5 \\ C_6H_5 \\ OH \end{matrix}$$

the structure of which appears from its very peculiar mode of formation. The authors propose reporting on this this compound in a following number.—*Berichte der Deutsch. Chem. Gesell.*, xxvii., p. 426.

NOTES ON ALUMINUM.*

By GEORGE FREDERICK ANDREWS.

The writer of this paper has made a large number of experiments with aluminum, particularly with reference to its use in jewellery, &c. The facts stated are the results of some of these experiments.

Alloys containing Gold.—The alloys of gold and aluminum are interesting, though of little practical use except for decorative purposes. The alloy with 6 per cent of gold is as white as pure aluminum, but much more brittle. The alloy with 10 per cent of gold is harder than aluminum, but does not work well, except at a high temperature. Its colour is light violet-brown. The alloy with 15 per cent of gold is a very soft fine-grained metal. It has a slight violet tint, although nearly white. The alloy with 50 per cent of gold has a beautiful violet colour. It is very soft and spongy. The alloy with 78 per cent of gold is very brittle. The colour is peculiar; it is between pink and violet. The alloy with 90 per cent of gold has a pale violet colour, while the alloy with 94 per cent of gold has a colour approaching pink again. Alloys containing small percentages of aluminum leave a bright violet colour on the cupel, under the blowpipe.

An alloy containing 50 per cent of gold, 45 per cent of copper, and 5 per cent of aluminum, takes the colour and polish of 14-carat gold, but easily tarnishes. This alloy has also been used in electroplating, but it is not entirely satisfactory for this purpose.

Alloys containing Silver.—Alloys containing from 4 to 8 per cent of silver, and from 96 to 92 per cent of aluminum, are useful for many purposes. They are harder than aluminum, but not brittle. They take a very fine polish, and hold it well. Their colour is very near that of fine silver. These alloys are now used for the manufacture of charms, medals, metal trimmings, and decorations of various kinds.

* Abstract from a Paper read before the Rhode Island Section, Feb. 15th, 1894. *American Journal of Science*, vol. xlvii., July, 1894.

Alloys containing Nickel.—The alloy containing 50 per cent of nickel and 50 per cent of aluminum has a dull gray colour. It is very porous, and so brittle as to be useless.

The following alloys of copper, nickel, and aluminum, are all very hard, fine-grained, and show great strength. The alloy containing 66 per cent of copper, 24 per cent of nickel, and 10 per cent of aluminum, takes a fine polish, and has the colour of 10-carat gold. The alloy containing 55 per cent of copper, 33 per cent of nickel, and 12 per cent of aluminum, has a beautiful golden brown colour. The alloy containing 72½ per cent of copper, 21½ per cent of nickel, and 6½ per cent of aluminum, closely resembles it, but the colour of the latter is richer and deeper. These alloys may become very useful for decorative purposes.

Solder for Aluminum.—Notwithstanding the assertions which are still heard to the contrary, aluminum can be successfully soldered. The writer has used solder which makes a clean, perfectly firm joint, and is in every way satisfactory. It requires no "soldering fluid" and no soldering iron.

Melting of Aluminum.—In melting aluminum the temperature should be kept even, and not much above the melting-point of the metal. The metal should be fed into the crucible in small pieces, and pushed down as fast as it becomes soft. The most serviceable flux is a little tallow, although it is not necessary to use any. A sand crucible must not be used, as the aluminum readily attacks the silicon.

In alloying, the aluminum should be put into the crucible after the other metal or metals have become liquid.

Restoration of the Mat.—Aluminum can be cleaned, and its peculiar mat restored by dipping for a minute and a quarter in a solution of 3 ounces of caustic potash in a quart of water, then washing thoroughly, and dipping in a mixture of three parts nitric and two parts sulphuric acid, by volume.

Caustic soda can be used with nearly as good results. The main advantage in the substitution is the lower price of caustic soda.

SPECIAL IMAGES OF THE SUN GIVEN BY SIMPLE RAYS CORRESPONDING TO THE DARK RAYS OF THE SOLAR SPECTRUM.

By H. DESLANDRES.

HITHERTO the surface of the sun has been studied merely with ordinary telescopes, refracting or reflective, the images of which are formed by the totality of the luminous or photographic rays. But as the continuous spectrum of the sun is furrowed by very numerous dark rays, the preceding images are due in great part to the simple rays of the brilliant intervals between the dark rays, rays which being united give merely a mean result. Thus I have already proposed (*Comptes Rendus*, Dec. 26, 1893) to study the sun with each ray, brilliant or dark, but isolated in order to recognise the successive layers of the sun and of its atmosphere which have been revealed at the margin by total eclipses, but which at ordinary times escape us, especially in the part projected on the disc. These strata of the sun by the play of their emissions and absorptions of light produce those inequalities of the spectrum which on the other hand may serve to disclose them.

I have the honour to present to the Academy the first results obtained in this novel manner. The apparatus employed consists of a siderostat, an ordinary object lens, and a registering spectrograph with two slits, which gives the image of any source in monochromatic light on the general principle established by M. Janssen in 1869.

1. *The Most Brilliant Rays.*—I have at first isolated with the spectrograph a brilliant interval between the dark rays; the image obtained, as it might be expected, is that of the ordinary telescope used alone. It shows the photosphere with the spots and the faculæ, which are especially brilliant at the margin. I have found merely that in the luminous region, the only one studied, the distinction between the brilliant ground of the disc and the spots and the faculæ is more marked for the more refrangible rays.

2. *Brilliant Rays of the Vapours of Calcium.*—They must be put aside, for they are reversed and given off by substances not liquid or solid, as in the former case, but gaseous and placed higher in the sun. They give with the spectrograph, as I have shown formerly, the image of the entire chromosphere of the sun as it would be seen isolated from the photosphere. The brilliant regions agree generally in form with the faculæ of the photosphere, but with the same brightness over the whole surface, at the centre as well as at the margin, and with a greater extension which often hides the spots the penumbra of which is in general not marked.

3. *Rays Relatively Sombre Corresponding to the Dark Rays.*—With the spectrograph employed the brilliant ray of calcium has a breadth of 0·06 m.m. to 0·07 m.m. But the broad dark ray of calcium, which includes in its midst the brilliant ray, is on each side at least 0·35 m.m. in breadth. But if we isolate with the second slit a part of the broad dark ray, we obtain, after a slightly longer exposure, a result curious and different. The brilliant regions of the facular flames still appear at the same points of the disc, but less intense with reference to the ground and less extended, sensibly of the same brightness at the centre and at the margin. The spots, on the other hand, appear distinct and not clouded, with their penumbræ well marked. I have still obtained images similar in their general lines with the other dark rays (iron, aluminium, calcium, carbon) sufficiently broad to be isolated with the spectrograph. Here is a new general fact peculiar to these dark rays.

These images of the dark rays are intermediate between the images of the photosphere and of the chromosphere. In fact they are given in great part by the solar strata productive of the dark rays, which probably belong to the photosphere as well as to the chromosphere, and which in any case occupy at least the lowest part of the chromosphere called by English writers *the reversing layer*. These strata appear, in fact, brilliant, and reversed in total eclipses during the two first seconds of the totality, according to the observations of Young. As they have a small height, at most a second of an arc, they are immediately hidden by the movement of the moon during the eclipses, and cannot be studied with the spectroscope at ordinary times. The images of the sun given by the simple radiations of the dark rays enable us to study the distribution and the intensity of the corresponding vapours which have so far escaped observation, and they open up thus a new track for research.

The spectrograph employed, which is that already described for photographing the chromosphere with the brilliant ray of calcium, is of too feeble a dispersion to permit the isolation of the very fine rays of the spectrum.

The vapours of calcium present a great interest on account of their triple inversion, which announces three different layers superimposed in height. The two lower layers corresponding to the broad dark ray and the double brilliant ray have been already obtained. It is requiste to search for the image of the third layer, the nearest to the corona, given by the small dark central ray. This last image, according to the results already furnished by the sectional spectrographs, will not present all the brilliant regions of the lower strata. It will permit us to create among the facular flames a distinction useful in the study of the solar atmosphere around the spots.—*Comptes Rendus*, cxix., p. 148.

CORRESPONDENCE.

EXAMINATION PAPERS.

To the Editor of the Chemical News.

Sir,—For some years it has appeared to me that it might be well, towards the end of summer, and, in fact, when opportunity offers, to subject the examination papers of the various examining boards to friendly criticism. Examiners are at present subjected to no court of censure, save that of the candidates, which as a rule does not reach the public ear; and yet unfair questions constitute a very real grievance, and one which has often a very prejudicial effect upon a young man's career. I know that we agree in thinking the excessive examination of the present day an evil; but, granting this, any course which will diminish the evil effect will tend towards good, and I am fortunate this year in having fewer criticisms to make than would have been the case in recent years.

Beginning with the examination of the Conjoint Board of the Royal Colleges, only one question, No. 5 in the July paper, calls for special remark. The question runs: "Solutions of phosphoric acid and boric acid are respectively neutralised with soda, and the two liquids evaporated. What is the composition of the crystals which separate in each case?" The answer to the first part of the question is obvious; but what about the second part? Can a solution of boric acid be neutralised with soda? The candidate in answering borax, the answer expected, would certainly be wrong.

In the University of London Examinations, the first question in the morning paper calls for comment. It is as follows:—

"Complete the following equations, giving the names of the interacting compounds and of the products:—

(i.) $Na_2HAsO_4 + AgNO_3$ =
(ii.) $Fe_2Cl_6 + Na_2CO_3$ =
(iii.) $Na_2HPO_4 + CaCl_2$ =
(iv.) $Sb_2S_3 + NaOH$ =
(v.) $Ca(OH)_2 + Cl_2$ = ."

It is to be remarked, first, that there is ambiguity about the statement of the question. Without the symbol "Aq," it should be taken for granted that in every case dry reactions are intended. This, however, is obviously not the intention of the examiners, except, perhaps, in (v.). Assuming, then, that it is intended that water shall be present, it is doubtful what is the product of equation (i.), whether Ag_3AsO_4 and free arsenic acid, or a certain amount of Ag_2HAsO_4. Precisely the same remarks apply to (iii.). Here all possible ortho-phosphates of calcium are doubtless formed, and in its presentment too little is known of their ratio to admit of statement in the form of an equation. The examiners probably imagine that ferric hydroxide would be precipitated in (ii.), but this is by no means the case. A basic carbonate of unknown composition is certainly formed. And I much doubt whether it should be expected of youngsters who have presumably spent a year at chemistry to know that the only two antimonites of sodium which have been prepared are—

$$NaSbO_2.3H_2O \text{ and } NaSbO_2.2HSbO_2;$$

and also that $NaSbS_2$ is the only known thioantimonite.

Had question (i.) been stated thus it would have been less objectionable: "What compounds do you suppose to be formed on adding a solution of disodium hydrogen arsenate to a solution of silver nitrate, &c.;" although it would then involve knowledge which is not usually gained until a much longer time has been spent in the study of chemistry. Indeed, angels would have feared to tread on such uncertain ground.

In the afternoon "Honours" paper for the same examination, a similar question occurs. It runs:—

"It is frequently stated that sulphuric acid is a 'stronger' acid than hydrochloric acid, silicic acid, or nitric acid. Discuss this statement, and mention reactions which tend to show that the expressions 'strong' and 'weak,' as applied to acids, are merely relative." This question, I fancy, would lead the candidate to suppose that the examiners believe that "the expressions 'strong' and 'weak,' as applied to acids, are merely relative;" that is, I imagine, that whether an acid is strong or weak depends on circumstances. Now I do not know what the examiners believe on this point, but one thing is very certain, viz., that each acid has its own particular strength, independent of other acids. It is measured by the amount of ionisation of the acid. The number of free ions in a solution of acid, of course, depends on the mass of the acid, on its dilution, on its temperature, and on the other constituents of the solution. But in comparing two acids it is implicitly understood, I fancy, that they shall be compared at the same temperature, that equal volumes of solution shall contain equivalent numbers of grm.-molecules, and that the disturbing bodies, if any are present, shall be the same. Unless such conditions are implied, no comparison of any kind can be made. When we say that Irishmen are stronger than Chinese, we implicitly assume that equal numbers of each race have their strength tested; not that 1000 Irishmen are stronger than 10 Chinese. Here I again have to make the comment that to answer the question involves more knowledge than such candidates are likely to possess; and, from the mode of statement, I should guess more than the examiners possess.

One more remark and I have done. Is it not a pity to perpetuate empirical names which are rapidly passing out of the language? "Red chromate of potassium," "glycocine," "taurine," are some of numerous examples. A man may be an excellent chemist, and yet fail to recognise "fuming spirit of Libavius," "Dutch liquid," or "Schlippe's salt."—I am, &c.,

W. Ramsay.

IMBIBITION OF EMBALMING FLUID.

To the Editor of the Chemical News.

Sir,—If any further evidence be needed to show that embalming fluid, externally applied, will pass through the unbroken skin, I should like to report having lately detected both the arsenic and zinc of such a fluid in the stomach of a man who had been "embalmed" by wringing out cloths in the fluid and laying them upon the face and chest. The circumstances of the case did not permit of any passage of liquid down the throat.—I am, &c.,

Wm. P. Mason.

Rensselaer Polytechnic Institute,
Department of Analytical Chemistry,
Troy, New York, July 20, 1894.

Quantitative Composition of the Creosotes of Beech and Oak.—A. Béhal and E. Choay.—Beech-creosote is richer in guyacol than that of the oak; the latter has a lower specific gravity, due to its larger percentage of monophenols, which render it more caustic.—*Comptes Rendus*, cxix., No. 2.

On a New Glucosane: Levoglucosane.—M. Tanret.—The formula of levoglucosane is $C_6H_{10}O_5$. It forms splendid crystals, very soluble in water and in ether. It melts at 178°, and sublimes unchanged if it is kept in fusion in a vacuum. It is lævorotatory, and its rotatory power in an aqueous solution at 10 per cent is $\alpha_D = -66{\cdot}5°$. Its specific gravity is 1·59 and its taste is slightly sweet. It does not ferment with beer yeast and does not reduce Fehling's liquid. It does not react with emulsine and it is not precipitated by basic lead acetate nor by ammonium-lead acetate. Its benzoic and acetic ethers have been obtained. With the acetic and benzoic acids glucosane behaves like triatomic alcohol.—*Comptes Rendus*, cxix., No. 2.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxix., No. 3, July 16, 1894.

New Researches on Chromium.—Henri Moissan.—This paper will be inserted in full.

On the Dimethyl- and Diethyl-amidobenzoylbenzoic Acids and on Dimethylanilinephthaleine.—A. Haller and A. Guyot.—The author has obtained dimethylamidobenzoylbenzoic acid in the form of fine yellow needles or lozenge-shaped crystals melting at 199°. It combines with acids and bases, forming two classes of salts, generally well crystallised. If in the preparation of dimethylamidobenzoylbenzoic acid we substitute diethylaniline for dimethylaniline we obtain the higher homologue of this acid. It forms slightly yellow crystals melting at 180° and having the properties of the dimethylated acid. If heated with diethylaniline and phosphorus trichloride it gives rise to diethylanilinephthaleine in acicular crystals.

On Certain Variations of Pneumobacillus Liquefaciens Bovis, the Microbe of the Contagious Peripneumonia of Oxen.—S. Arloing.—There are two varieties of the pneumobacillus and not two distinct microorganisms. The pathogenic properties of the non-liquefying variety are less accentuated.

Separation and Determination of Tin and Antimony in an Alloy.—M. Mangin.—This paper will be inserted in full.

On Rotatory Powers Variable with the Temperature: A Reply to M. Colson.—M. A. Le Bel.—In this controversial paper the author ascribes the results obtained by M. Colson to reactions ensuing among impurities present.

Synthesis of Mesoxalic Acid and Bismuth Mesoxalate.—H. Causse.—The reaction of glycerin with concentrated nitric acid can be regulated by the presence of a metallic oxide capable of forming an insoluble metallic compound with the nascent acid. The author treats glycerin with neutral bismuth nitrate.

Contribution to the Study of certain Amidic Acids Obtained by Splitting up Proteic Vegetable Substances.—E. Fleurent.—Since we know that vegetable albumen and legumine yield aspartic acid in appreciable proportion we are entitled to conclude that in the conditions of the experiment this acid, and perhaps its analogues, are split up, producing a quantity of ammonia, which is added to the proportion furnished by the hydration of the carbamic and oxamic groups, and at the same time a corresponding quantity of oxalic acid, and not carbonic acid, breaks the equilibrium established in the case of the animal albumenoids. The transformations of the aspartic and glutamic acids appear as a new fact in the history of the amido-acid compounds. In presence of the facts observed it is evident that the constitutional formula admitted for aspartic acid cannot explain the mechanism of the splitting up observed.

On some Derivatives of the Propylamides.—F. Chancel.—Propylpropylidenamine, $C_3H_6 = N - C_3H_7$, is obtained by the action of propionic aldehyd upon monopropylamine. It is a colourless, mobile liquid, of a very disagreeable ammoniacal odour, boiling at 102° under a pressure of 760 m.m. Its density at 0° is 0·84. It is very sparingly soluble in water.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. ix., No. 101.

Report made by M. Vieille on Behalf of the Committee of Chemical Arts on the Work of M. Daniel, entitled: "The Industrial Explosives, Fire-damp, and Coal-dust.—The first part of the work is a brief account of the properties of explosives and the methods of their employment. He explains the methods in use for determining *a priori* their industrial yield, and he shows thei imperfection of the methods in use. We do not know with even approximate completeness the manner in which the various resistant media behave when the properties of the explosive vary. The problem of the adaptation of an explosive to a given useful effect has still to be solved. The second part of the work concerns the employment of explosives in inflammable media.

Steel and Iron Wires.—J. P. Bedson.—This paper is taken from *Engineering*.

Exhibition of Urban and Maritime Hygiene and of Hydrotherapie.—This Exhibition opened at Boulogne on July 15, and will close on September 15. It is held at the Quai Gambetta.

International Exhibition at St. Petersburg.—This display will take place in the autumn, and will include fruits, vegetables, wines, ciders, perries, brandies, machines, and alimentary products, under the patronage of the Czar. Several grand special prizes and extraordinary rewards will be awarded in all the nine sections.

No. 102.

Report Presented by M. Biver on Behalf of the Committee of Chemical Arts on a New Elevator for Liquids by means of Compressed Air, devised by Paul Kestner, Technical Chemist, of Lille.—The principle of the Kestner elevator consists in the use of a bell-shaped floater fitted within with a valve commanding the access of compressed air. The construction of the apparatus cannot be made intelligible without the use of the three accompanying figures.

Patent-Law Reform.—At the Edinburgh meeting of the Society of Chemical Industry, the President, Mr. E. C. C. Stanford, in his discourse, pointed out as a capital defect of the patent system that aliens can obtain and uphold a British patent without ever working such or allowing it to be worked in these realms. Thus, as Mr. Stanford expressly puts it, the law is made the means not of introducing new arts into the country, but of preventing their introduction. This is almost verbally the view which has been repeatedly maintained in the CHEMICAL NEWS.

Condensation of Aldehyds and Cyanides. — C. Bechert.—In this memoir the author studies the action of formaldehyd upon ethylencyanide, that of benzaldehyd upon ethylencyanide both in the cold and in heat, the condensation of anisaldehyd and ethylencyanide, and the condensation of aldehyds with cyanacetic esters. It appears from the author's results that the condensations of ethylencyanide and aldehyds take place differently according to the conditions, but in no instance have products been obtained of the composition expected, *i.e.*,—

$$\begin{matrix} CR''.CN \\ | \\ CH_2.CN \end{matrix} \quad \text{or} \quad \begin{matrix} CR''.CN \\ | \\ CR''.CN \end{matrix},$$

but it appeared that, along with the condensation with the aldehyd in question, water was always taken up. Cyanacetic ester, however, condenses in most cases readily with the aldehyds employed in the manner expected.—*Journal fur Praktische Chemie*, Nos. 13-14.

MISCELLANEOUS.

Mr. Charles E. Cassal, F.I.C., Public Analyst for Kensington and St. George's, Hanover Square, has been elected Honorary President of the VIIth (Food) Section of the forthcoming International Congress of Hygiene and Demography at Budapest.

City and Guilds of London Institute.—The Council of the City and Guilds of London Institute have conferred the Fellowship of the Institute upon Dr. W. E. Sumpner, who was awarded the Diploma of Associate of the Institute in 1887, and has since by many original and valuable researches contributed to the advancement of the Electrical industry.

The Pollution of Rivers as Injurious to Fish.—The German Fisheries Association (Fischerei-Verein) offers prizes for the following investigations:—

I. Simple, certain, and universally applicable methods of determining in waters, oxygen, carbonic acid, and nitrogen. Up to June 1st, 1895. Prize, 800 marks.

II. Investigations on the pathological-anatomic detection of the action upon fishes of the following groups of substances present in waste waters:—

1. Free acids.
2. Free bases, especially lime, ammonia, and soda (also potassium and sodium carbonates).
3. Free bleaching gases (chlorine and sulphurous acid).
4. Determination of the pathological characteristics of death by suffocation in fishes. Up to Nov. 1st, 1896. Prize, 1000 marks.

III. Development and vital conditions of the water fungus, *Leptomitus lacteus*, with especial reference to its appearance and disappearance in polluted waters. Up to Nov. 1st, 1895. Prize, 600 marks.

The treatises may be written in German, French, or English. They are to be forwarded to Prof. Dr. Weigelt, Berlin, S.W., Zimmerstrasse, Nos. 90 and 91.—*Chemiker Zeitung.*

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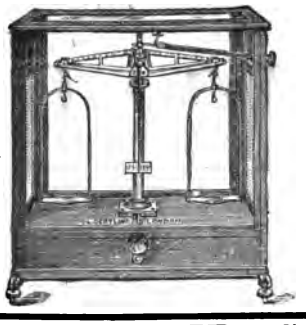

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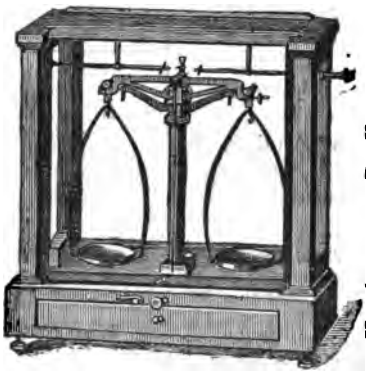

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ADDRESS TO THE CHEMICAL SECTION OF THE BRITISH ASSOCIATION.

Oxford, 1894.

By Professor H. B. DIXON, M.A., F.R.S., President of the Section.

"*An Oxford School of Chemists.*"

It has been said, and no doubt with truth, that few Presidents of Sections start writing an address without referring to that of their predecessor who held office on the last occasion when the Association met in the same city. By such reference each new President gains the advantage of many points of perspective and contrast; for in the interval a generation of workers has passed away, and the last new thing of the old meeting is the ancient instance of to-day. In the present case I turned to the Report of 1860 with a lively hope of drawing inspiration from it; for my predecessor at the last Oxford meeting was no less a master of experiment and expression than the late Professor Brodie. Judge of my disappointment when I found that Brodie had written no address at all. Whether that great man, knowing there were better things to do here than listen to addresses, had the courage to make an innovation he thought desirable in itself, or whether, as others say, he was but obeying the etiquette of the Oxford professoriate—the fact remains the assembled chemists went away unaddressed, and the natural spring of inspiration for the address of 1894 is found dry at its source. Of course, you will say, "Why do you not follow such a good example?" I wish I had the courage. As it is, I can but urge the vacuum of 1860 as some excuse for the emptiness of the address I now present—compelled to do so partly by the force of fashion and the demands of the assistant general secretary, and (shall I add?) partly by the gratification of holding forth, with a little brief authority, in my old academic home, endeared to me personally by so many happy memories, and hallowed in the minds of chemists by the traditions of such great achievements in the science we pursue.

I say *traditions* advisedly, for the chemical achievements spoken of were largely forgotten, or put on one side as guesses and half-truths. No chemist here will need reminding that I refer to *the first school of scientific chemistry*, the school founded two centuries and a half ago by Robert Boyle with his disciples Hooke and Mayow—a group whom I will venture to call "the Oxford school of chemists." And now that chemists are met together once more in Oxford it seemed to me not inappropriate for us to consider what this school of chemists accomplished, and wherein it failed, what led to the sudden growth and what to the decline of chemical investigation here, and what lessons for modern Oxford may be read in the history of that rise and fall.

The intellectual awakening which followed the re-discovery of the ancient world of literature gave rise to the scientific interrogation of nature. In Italy first and then in France, England, and in Germany, the diffusion of classical learning broke down the ancient barriers of restraint, and developed a spirit of free inquiry. It was not so much that ignorance had to be dispelled, but that the right of search had to be established. Here and there during the Middle Ages some man of genius had arisen—learned beyond all his contemporaries, intrepid in the pursuit of truth—only to be crushed by a political and mental despotism. The name of Roger Bacon arises at once in our thoughts, who from his Oxford cell sent forth that great appeal for experimental science that nearly converted a Pope of Rome and won three centuries for intellectual freedom. But his labour bore no fruit. I know no better index to the dominant sentiment of the time than the following words from a papal rescript reproving the members of an Italian university for scientific presumption:—"They must be content with the landmarks of science already fixed by their fathers, and have due fear of the curse pronounced against him who removeth his neighbour's landmark." Under such conditions no wonder philosophy was at a standstill. "The same knots were tied and untied; the same clouds were formed and dissipated" (Whewell, "Hist. of Ind. Sci."). The cramped philosophy of the Middle Ages had its alchemy a fitting colleague—with its mysticism, its sordid ideals, its trickery, and its arrogance. The revival of learning was thus an emancipation of the mind, and in the new freedom the sciences of mechanics, physics, and chemistry arose. The first necessity for progress was enlightenment, the second was experiment; in the year that Francis Bacon died Robert Boyle was born.

The common pursuit of experimental inquiry and the need for constant criticism and discussion among its followers led to the foundation of scientific societies. Such societies, which have greatly influenced the progress of knowledge, sprang up in Florence and Padua, in Paris and Oxford—wherever, among bodies of learned men, some were found in sympathy with natural philosophy. Among these associations the Philosophical Society of Oxford has played no unimportant part, and, however much Oxford may have undervalued its work, for one thing all chemists are grateful, and Oxford herself may feel proud—that here, under her influence, first grew up the idea that chemistry was no mere drudge of medicine, or genii of the alchemist, but a science to be studied purely for itself.

The origin of this Oxford Society has been well told by Dr. Wallis, one of its founders:—

"About the year 1645, while I lived in London (at a time when, by our civil wars, academic studies were much interrupted at both Universities), besides the conversation of eminent divines, I had the opportunity of being acquainted with divers worthy persons inquisitive into natural philosophy, and particularly of what hath been called experimental philosophy. We did by agreements meet weekly in London to treat and discourse of such affairs; of which number were Dr. John Wilkins, Dr. Jonathan Goddard, Dr. Ent, Dr. Merret, Mr. Samuel Foster, then Professor of Astronomy in Gresham College, and Mr. Theodore Haak, and many others.

"These meetings we held sometimes at Dr. Goddard's lodgings, on occasion of his keeping an operator at his house for grinding glasses for telescopes and microscopes; sometimes at a convenient place in Cheapside, and sometimes at Gresham College. Our business was (precluding matters of theology and State affairs) to discourse and consider of philosophical inquiries. . . . About the year 1648, some of our company being removed to Oxford (first Dr. Wilkins, then I, and soon after Dr. Goddard), our company divided. Those in London continued to meet there as before, and those of us at Oxford, with Dr. Seth Ward (since Bishop of Salisbury), Dr. Ralph Bathurst, President of Trinity College, Dr. Petty, Dr. Willis (an eminent physician in Oxford), and divers others, continued such meetings in Oxford, and brought those studies into fashion there, meeting first at Dr. Petty's lodgings (in an apothecarie's house), because of the convenience of inspecting drugs, and, after his removal, at the lodgings of Dr. Wilkins, then Warden of Wadham College, and, after his removal, at the lodgings of the Honourable Mr. Robert Boyle, then resident for divers years in Oxford."

Robert Boyle, the youngest child of the great Earl of Cork, was born at Lismore in 1626. His mother died when he was a child. Always delicate, he was sent at

twelve years of age with a tutor to the Continent; he remained abroad for six years. He studied chiefly at Geneva and at Florence, where he read the works of Galileo. Returning to England, in 1644, he busied himself with chemistry at Stalbridge, a manor in Dorsetshire left him by his father. On his visits to London he became one of the members of the "Invisible College," the germ of the Royal Society. "Vulcan has so bewitched me," he writes at the age of twenty-three, "as to make me fancy my laboratory a kind of elysium."

Drawn to Oxford in 1654, Boyle spent here the most active years of his life in experimental research. Of Boyle's scientific writings much has been said in extravagant praise and much in ridicule. Boerhaave wrote:—"To him we owe the secrets of fire, air, water, animals, vegetables, and fossils." This phrase is not more grotesque than that of a recent writer, who says, "Boyle's name is identified with no great discovery." Dr. Johnson has very justly remarked, in a number of the *Rambler*:—"It is well known how much of our philosophy is derived from Boyle's discoveries, yet very few have read the details of his experiments. His name is indeed reverenced, but his works are neglected." It is, indeed, rather hard to read through one of Boyle's papers, even in the abridged form. Though clear, they are discursive. The writer cannot rid himself entirely of the essences and qualities of the alchemists; and it is only when we compare these records with the works of Van Helmont, his immediate predecessor, that we recognise the enormous advance that has been made by Boyle. I must pass over his physical work on the elasticity of the air. It must suffice to say that he established by most careful experiment the law which is known by his name—that the volume of a given mass of air varies inversely as the pressure upon it. He determined the density of the air, and pointed out that bodies altered in weight according to the varying buoyancy of the atmosphere. One of his most important chemical papers—certainly the one most frequently cited—is "The Sceptical Chemist," published anonymously in 1661. I will attempt the briefest account of it. The opening words of the dialogue strike the keynote of the whole:—

"Notwithstanding the subtle reasonings of the Peripatetics and the pretty experiments of the Chymists, I am so diffident as to think that, if neither can produce more cogent arguments than are usually given, a man may reasonably doubt as to the number of those material ingredients of mixed bodies which some call elements and others principles." He proceeds, through the mouth of one of the supposed disputants, to attack the doctrine of the three elements, the *tria prima* of the alchemists—sulphur, mercury, and salt. "There are some bodies," he says, "from which it has not yet been made to appear that any degree of fire can separate either salt, or sulphur, or mercury, much less all the three. Gold is the most obvious instance. It may be heated for months in a furnace without losing weight or altering in character, and yet one of its supposed constituents is volatile and another combustible. Neither can water or solvents separate any of the three principles from gold; the metal may be *added to*, and so brought into solution and into crystalline compounds, but the gold particles are present all the time; and the metal may be reduced to the same weight of yellow, ponderous, malleable substance it was before its mixture." He points out the confusion which earlier chemists had made between calcination in the open air and distillation in retorts; he shows that in compounds, *e.g.*, copper nitrate, the particles retain their nature, although disguised, in the combination, for the nitric acid may be separated by heat, the copper by precipitation, but the sceptical chemist, though pouring ridicule on the *tria prima*, could not but admit the power of water to produce organic substances. He quotes Van Helmont's famous experiment of growing a shoot of willow in baked earth moistened with distilled water, and he repeats the experiment in various forms. Ignorant of the existence of carbonic acid in the air (discovered a century later by Black), he is driven to conclude that the plant is fashioned out of the pure water. But he rejects the doctrine—as old as Thales and as modern as Van Helmont—that water is the foundation of all things. M. de Rochas had published a remarkable experiment on water. By artificial heat, by graduations of coagulations and congelations, he had turned it into earth which produced animals, vegetables, and minerals. The minerals began to grow and increase, and were composed of much salt, little sulphur, and less mercury; the animals moved and ate, and were composed of much sulphur, little mercury, and less salt. "I have some suspicions," says Boyle, "concerning this strange relation; though as for the generation of living creatures, both vegetable and sensitive, it need not seem incredible, since we find that our common water, which is often impregnated with a variety of seeds, long kept in a quiet place, will putrefy, and then, too, produce moss and little worms according to the nature of the seeds that were lurking in it."

I will give two short quotations from the "Sceptical Chemist," which show the author at his best and at his worst. In the first he is discussing the nature of chemical combination between elementary particles: "There are clusters wherein the particles stick not so close together, but they may meet with corpuscles of another denomination, disposed to be more closely united with some of them than they were among themselves; and in such case two corpuscles thus combining, losing that shape, size, or motion upon whose account they exhibited such a determinate quality, each of them really ceases to be a corpuscle of the same denomination as it was before; and from the coalition of these there may result a new body, as really one as either of the corpuscles before they were confounded. . . . If you dissolve minium in good spirit of vinegar and crystallise the solution, you shall not only have a saccharine salt exceedingly different from both its ingredients, but the union is so strict that the spirit of vinegar seems to be destroyed, . . . for there is no sourness at all, but an admirable sweetness to be tasted in the concretion." In this passage we can distinctly see the germ of the modern theory of chemical affinity uniting atoms into chemical compounds. In the second quotation Boyle is arguing that fire is not only an analyser of mixtures, but compounds the ingredients of bodies after a new manner; mercury, for instance, may be turned into a liquid, from which the mercury cannot be reduced again, and consequently is more than a 'disguise' of it. Two friends of mine," he says, "both of them persons of unsuspected credit, have solemnly assured me that after many trials they made to reduce mercury into water, they once, by several cohobations, reduced a pound of quicksilver into almost a pound of water, and this without the addition of any substance, but only by urging the mercury with a fire skilfully managed. Hence it appears that by means of fire we may obtain from a mixed body what did not pre-exist therein." Boyle has sometimes been charged with credulity, and chemists who know how mercury has a way of disappearing without leaving even its weight of water behind will smile to hear that the persons of unsuspected credit responsible for this experiment were "the one a physician, the other a distinguished mathematician."

Boyle's writings contain the record of numerous important chemical observations, *e.g.*, the synthesis of nitre, and the preparation of nitric acid by the distillation of nitre with oil of vitriol. He discovered several of the delicate tests we still use, *e.g.*, solution of ammonia as a test for copper, silver nitrate as a test for chlorides, gallic acid as a test for iron. But I wish especially to refer to the work done by Boyle on the air and its relation to combustion. The air, according to him, was composed of three different kinds of particles: (1) Exhalations from water and animals; (2) a very subtle emanation from the earth's magnetism, which produces the sensation of light; and (3) a fluid compressible and dilatable, having weight,

and able to refract light. It is this third portion of air which plays an active part in many chemical operations. Like Van Helmont, Boyle recognised differences in gases, but did not distinguish them as being something different in kind from air. He prepared hydrogen by the action of hydrochloric and sulphuric acids on iron, but his chief concern was to show that the new gas was compressible and was dilatable by heat; in other words, that it was really *air*. His observations are worth quoting; they contain, I believe, the first undoubted description of hydrogen, and the first method devised for collecting and examining freshly-prepared gases:—

"Having provided a saline spirit, . . . exceedingly sharp and piercing, we put into a viol a convenient quantity of filings of steel, purposely filed from a piece of good steel. This metalline powder being moistened with the menstruum was afterwards drenched with more, whereupon the mixture grew very hot, and belched up copious and stinking fumes. . . . Whencesoever this stinking smoak proceeded, so inflammable was it, that upon the approach of a lighted candle it would readily enough take fire, and burn with a blewish and somewhat greenish flame at the mouth of the viol; and that, though with little light, yet with more strength than one would easily suspect."*

And again: "We took a clear glass vial, capable of containing three ounces of water, with a long cylindrical neck; this we filled with oil of vitriol, and fair water, of each a like quantity, and casting in six small iron nails we stopped the mouth of the glass, and speedily inverting it, we put the neck of it into a wide-mouthed glass with more of the same liquor in it. . . . And soon after we perceived the bubbles, produced by the action of the menstruum upon the metal, ascending in swarms; by degrees they depressed the liquor till, at length, the substance contained in these bubbles possessed the whole cavity of the vial. And for three or four days and nights together the cavity of the glass was possessed by the air, since by its spring it was able for so long a time to hinder the liquor from regaining its former place. Just before we took the vial out of the other glass, upon the application of the warm hand to the convex part of the glass, the imprisoned substance readily dilated itself like air, and broke through the liquor in several succeeding bubbles."

The importance of this experiment will be evident when we consider that Van Helmont had declared that gases could be made artificially in many ways, but could not be caught and held in vessels.†

Armed with the air-pump which he had so greatly improved, Boyle in 1660 began many experiments on combustion, which he afterwards published under the title "New Experiments touching the Relation betwixt Flame and Air." In these researches he shows that sulphur will not burn when the air is removed. The sulphur was lowered on to a hot iron plate in a receiver made vacuous by the pump; it smoked, but did not ignite. On allowing a little air to enter "divers little flashes could be seen"; these were extinguished on sucking out the air again. A candle flame and a hydrogen flame under a receiver were gradually extinguished when the air was pumped away. On the other hand, on dropping gunpowder on to a hot iron plate *in vacuo* there appeared a "broad blue flame like that of brimstone, which lasted so very long we could not but wonder at it;" and fulminating gold detonated *in vacuo* when heated by a burning glass, or when dropped on heated iron. Gunpowder also he found to burn under water. He is driven to the conclusion "that flame may exist without air." But it may be supposed that air is mechanically enclosed in the crystals of nitre—"in its very formation the corpuscles may intercept store of little aereal particles. . . . According to this surmise, though our mixture burns under water, yet it does not burn without air, being supplied with enough to serve the turn by the numerous eruptions of the aereal particles of the dissipated nitre." However, he "removes this suspicion" by obtaining nitre crystallised *in vacuo*. He then suggests the possibility of the nitre supplying "vehemently agitated vapours" which are no true air, but being exceedingly rarefied by the fire "emulate air." Boyle never grasped the true function of air in combustion. From his later experiments on the calcination of metals he drew the same conclusion that we find in the "Sceptical Chemist," namely, that igneous particles combine with other corpuscles to form new bodies. And yet he saw there was a real connection between air and fire. In his tract on "Artificial Phosphori," Boyle showed that a piece of phosphorus sealed up in a glass vessel gradually lost its light. "It seems," he wrote, "that the air included with the phosphorus either had some vital substance preyed upon thereby, or else was tamed by the fumes of the phosphorus and rendered at length unfit to continue the particular flame of our noctiluca."

The genius of Robert Hooke was in sharp contrast with that of Boyle. Quick, restless, imaginative, he sprang from discovery to discovery. With extraordinary acuteness and powers of invention, he lacked the steady purpose of Boyle, the calm judgment and completeness of Newton—his two great scientific contemporaries. It might be said of Hooke, as was said of a great poet, he touched nothing he did not strike fire from; and some would add that his touch had the same effect on persons as on things. We can hardly name a discovery of this age which Hooke had not in part anticipated and claimed as his own. Like a prospector in a newly-discovered mining district, he hurried from spot to spot, pegging in his claims and promising to return to work out the ore. And what rich lodes he struck! The particular claim we are concerned with here is the discovery of the relation between air and flame. In 1665 Hooke published in the *Micrographia* a description of flame and the phenomena of combustion which in my judgment has never been surpassed. How far he was indebted to Boyle will appear directly.

Born in 1635, Hooke spent five years at Westminster School, then under Dr. Busby, and proceeded to Christ Church in 1653. At school and college it is related of him that he devoted his time to designing flying machines. These mechanical inventions attracted the notice of Dr. Wilkins, Warden of Wadham, and a leading member of the Philosophical Society. This led to his introduction to Dr. Willis, to whom he became assistant in chemistry and natural philosophy. Willis recommended him to Boyle, whose assistant he became. His first work in Boyle's laboratory was the construction of the improved air-pump. In 1662 Boyle obtained for him the position of curator of experiments in the London Society, soon to be known as the Royal Society. Hooke was thus Boyle's assistant when those experiments on combustion I have described were being carried on. Among other experiments made by Boyle were some on the distillation of wood in retorts.

"Having sometimes distilled such woods as box, whilst our *caput mortuum* [*i.e.*, the residue] remained in the retort it continued black like charcoal, though the retort were kept red-hot in a vehement fire; but as soon as ever it was brought out of that vessel into the open air the burning coals would degenerate or fall asunder into pure white ashes" ("The Sceptical Chemist"). Hooke saw the experiment and a new light flashed on him. "From the experiment of charring coals," he writes, "(whereby we see that, notwithstanding the great heat, the solid parts of the wood remain, whilst they are preserved from the free access of the air, undissipated) we may learn that which has not been published or hinted, nay, not so much as thought of by any; and that in short is this:—

"That the air is the universal dissolvent of all sulphurous [*i.e.*, combustible] bodies. . . .

* "On the Difficulty of Preserving Flame without Air," 1672.

† "Gas, vasis incoercibile, foras in aerem prorumpit."—*Ortus Medicinæ*. The epithet "sylvestre" was applied by Van Helmont to all artificially prepared gases. He meant by it "untameable" and "non-condensible"—"quod in corpus cogi non potest visibile."

"That this action of dissolution produces a very great heat, and that which we call fire.

"That this action is performed with so great a violence, and does so rapidly agitate the smallest parts of the combustible matter, that it produces in the diaphanous medium of the air the action, or pulse of *Light*.

"That this dissolution is made by a substance inherent and mixed with the air, that is like, if not the very same with, that which is mixed in saltpetre.

"That the dissolving parts of the air are but few, . . . whereas saltpetre is a menstruum . . . that abounds more with these dissolvent particles.

"It seems reasonable to think that there is no such thing as an element of fire, . . . but that that shining transient body which we call flame is nothing else but a mixture of air and volatile parts of combustible bodies, which are acting upon one another whilst they ascend; which action . . . does further rarifie those parts that are acting or are very near them, whereby they, growing very much lighter than the heavy parts of that *menstruum* that are more remote, are thereby protruded and driven upwards."

Hooke quotes no other experiments in support of his theory of flame. He states that he has made many; he has, however, only time "to hint an hypothesis," which if he is permitted opportunity he will "prosecute, improve, and publish." Some years later he returned to the subject of flame in his tract called "Lampas," published in 1677. "The flame, as I formerly proved, being nothing but the parts of the oyl rarified and raised by heat into the form of a vapour or smoak, the free air that encompasseth this vapour keepeth it into a cylindrical form, and by its dissolving property preyeth upon those parts of it that are outwards, . . . producing the light which we observe; but those parts which rise from the wick which are in the middle, are not turned to shining flame till they rise towards the top of the cone, where the free air can reach and so dissolve them. With the help of a piece of glass anyone will plainly perceive that all the middle of the cone of flame neither shines nor burns, but only the outward superficies thereof that is contiguous to the free and unsatiated air."

What is practically the same theory of flame was worked out experimentally by John Mayow, Fellow of All Souls: this was published a few years after the "Micrographia."

But Mayow went further, and distinctly showed the dual nature of the air. One constituent of air, the nitre air, is concerned in respiration and combustion; the other will neither support flame nor animal life. The ideas, the names, proposed by Hooke and Mayow, are so exactly similar that it is impossible to imagine that the work was done independently. The two were working at the same time at Oxford, and Mayow, having been an undergraduate at Wadham under Dr. Wilkins, became the pupil of Willis. Yet Mayow nowhere mentions Hooke's name. A writer in the "Dictionary of National Biography" (Mr. P. J. Hartog) has shrewdly observed that Hooke has brought no charge of plagiarism against Mayow, and even proposed him for the Royal Society four years after the publication of the "Five Tracts." Knowing what we do of Hooke's jealousy, it seems exceedingly unlikely that Mayow was merely working out Hooke's ideas. It seems to me probable that Hooke and Mayow worked together under Boyle between 1660 and 1662; that in Boyle's laboratory they saw and assisted in the experiments which led them jointly to their theory; that Hooke, busy with other work in London, published the hypothesis in 1665 without further verification; and that Mayow in Oxford systematically worked through the experiments on which he based his conclusions.

Let me briefly show what the experiments were on which Mayow relied. Combustible bodies will not burn in the vacuous receiver of Boyle's air-pump; they will burn *in vacuo* or under water when mixed with nitre. There is, therefore, something common to air and to nitre which causes combustion. The fiery particles in air and in nitre both form oil of vitriol by their union with sulphur; they both form iron vitriol by their union with pyrites. Rust of iron is produced both by the air and by acid of nitre; the acids of sugar and honey are formed, and wine is soured, in the same way. The nitre-air (spiritus nitro-aëreus), the supporter of combustion and the acid producer, is therefore the same chemical substance whether it exist in the gaseous form in air or is condensed in saltpetre.

Mayow heated a weighed quantity of antimony by means of a burning glass, and found it increased in weight during the calcination;* the calcined antimony, he adds, has the same properties as the body prepared by heating antimony with nitric acid; it is impossible to conceive, he says, whence the increase in weight arises except by the fixation of the particles of nitre-air during the heating.

The nitre-air does not make up the whole of the air, but only its more active and subtle part, for a candle under a glass will cease to burn while there is still plenty of air left. The experiment by which Mayow shows this is so important that I will quote his words:—

"Let a lighted candle be so placed in water that the burning wick shall rise about six fingers' breadth above the water; then let a glass vessel of sufficient height be inverted over the candle. Care must be taken that the surface of the water within the glass shall be equal in height to that without, which may be done by including one leg of a bent syphon within the vessel while the other opens outside. The object of the syphon is that the air, enclosed by the vessel and compressed by its immersion into the water, may escape through the hollow syphon. When the air ceases to issue, the syphon is immediately withdrawn, so that no air can afterwards get into the glass. In a short time you will see the water gradually rising into the vessel while the candle still burns."

In other experiments he burnt camphor and sulphur supported on a shelf in the inverted vessel. The water rose, he says, because, owing to the disappearance of the fire-air, the air left could not resist the pressure of the atmosphere outside. When the combustibles were extinguished it was impossible to kindle them again by means of the sun's rays concentrated on them by a burning glass. The residual air was no more able to support combustion than the vacuum of Boyle's engine. Again, the respiration of animals in the closed space was shown to diminish the air, and to render it incapable of supporting combustion; the fire-air was as necessary for life as for flame. The larger portion of the air was something entirely different from fire-air, and incapable of supporting life or combustion. I believe this to be the first definite statement founded on experiment that the air is composed of two distinct gases.

I have given the fundamental facts in chemistry we owe to Mayow; the limits of his work are sufficiently obvious. He detected the existence of what we call oxygen gas in the air, and demonstrated some of its most remarkable properties. He did not isolate the gas, or show what became of it in combustion; he did not always distinguish between the gas itself and the heat produced by its action. But the advance he made was extraordinary—not so much in the conclusions he drew as in the experiments and arguments he founded them on. Compare him for a moment with another writer who had previously expressed similar views concerning the calcination of metals. Jean Rey, of Perigourd, a witty and shrewd physician, published in 1630 a series of essays attributing the increase in weight of metals on calcination to the fixation of the air. "When asked," he writes, "why tin and lead increase in weight on calcination, I reply and gloriously maintain that this increase comes from the air which is thickened and made heavy and adhesive by the

* This experiment seems to have been first described by Poppius, 'Basilica Antimonii," 1625.

long continued heat of the furnace. This air mingles with the calx and attaches itself to the smallest particles." The reply is good, but the reasons that gloriously maintain it are not altogether conclusive. I can only give two of them: (1) *The air has weight.*—This is shown by the increase in velocity of heavy bodies falling to the earth, because as the body approaches the earth it subtends a wider angle from the centre of the earth, and receives more shocks from the particles of air. Again, although the air appears to weigh nothing on the balance, this is because we weigh it in air; it loses its weight, just as water weighs nothing in water. Fire has weight too, and should we ever find ourselves in a region where fire is the predominant element, we shall be able to prove the statement, in the same way. (2) *Fire can thicken and make air heavy.*—Stand a cannon upright and put a red-hot ball into it. You must admit that the air in the gun is so small in quantity that it will be heated to the same temperature as the ball. Nevertheless you can hold your hand in the mouth of the gun at first, but in a short time you cannot do so. Not that the air has got hotter, it is cooling all the time; it is because the air is thickened. Now if you drop a fleece of wool into the mouth, it will not descend, and if you push it in it will come up again, proving the air is heavier. Lastly, the air is seen to tremble over the mouth of the gun, and objects seen through it are blurred. This is due to the thickening, it cannot be due to a motion of the air; "for I see," he says, "a lady's beauty quite distinctly through the air she flutters with her fan."

From what has been stated it will be clear that the Oxford School of Chemistry was a *school of research*. Boyle gave no instruction in the ordinary sense; and, indeed, had no official connection with the University. But that he thought instruction in chemistry should be given in the University is obvious from the fact that he brought over a chemist from Strasburg, and set him up as a lecturer, with rooms next his own and the use of his laboratory. Of these lectures we find a quaint account in Anthony Wood's diary:—

"An. Dom. 1663.

"Began a course of chemistry under the noted chemist and rosicrucian, Peter Sthael, of Strasburgh, brought to Oxon. by the Hon. Mr. Rob. Boyle, an. 1659. He took to him scholars in the house of John Cross next on the w. side to University Colle. The club consisted of 10 at least, whereof Francis Turner of New Coll. was one, Ben Woodroff of Ch. Ch. another, and John Lock of the same house, afterwards a noted writer. This John Lock was a man of turbulent spirit, clamorous and never contented. The club wrote and took notes from the mouth of their master, who sat at the upper end of the table, but the said J. Lock scorned to do it; so that while every man besides were writing, he would be prating and troublesome. After the beginning of the year 1663 Mr. Sthael removed his elaboratory to a draper's house, called John Bowell, afterwards mayor of the city, situate in the parish of All Saints. He built his elaboratory in an old hall in the back, for the house itself had been an ancient hostle; therein A. W. and his fellows were instructed. The chemical club concluded, A. W. paid Mr. Sthael 30 shill: having paid 30 shill: beforehand. A. W. got some knowledge and experience, but his mind still hung after antiquities and musick."

In spite of Boyle's privats position, his blameless life, his devoutness, and his charity, his work aroused bitter animosity in Oxford. He was attacked in the University pulpit, in public orations, in private squibs; his theories were described as destructive of religion, his experiments as undermining the University. But what chiefly drew the indignation of his opponents was that he, a gentleman by birth and fortune, should concern himself with low mechanical arts. Against these attacks Boyle replied with irresistible logic. His vindication of the nobility of scientific work constitutes one of his greatest claims on our gratitude.

Boyle left Oxford in 1668. Mayow died in 1679. In 1683 Anthony Wood informs us that "the Oxford elaboratory was quite finished"; but the impulse given to the study of Chemistry in Oxford gradually died out. I do not know the history of the Chair of Chemistry in Oxford (if there was one) in the eighteenth century. Richard Frewin, of Christ Church, is described as Professor of Chemistry in 1708. He does not seem to have taken himself too seriously in this capacity. Uffenbach, who visited Oxford in 1710, says he found the stoves in fair condition, but everything else in the laboratory in dirt and disorder. Frewin himself was elected Camden Professor of Ancient History in 1727. He seems to have thrown himself into his new work with great ardour; for Hearne relates that, on his election, he at once bought one hundred pounds' worth of books in chronology and history to fit himself for his duties. For a companion picture to this we may glance at the appointment in 1764 of Richard Watson (afterwards Bishop of Llandaff) to the Chair of Chemistry at Cambridge, which had been founded in 1702. Dr. Watson, we are told, knew nothing at all of chemistry; had never read a syllable nor seen a single experiment on the subject. On his election he sent to Paris for an "operator," and set to work in his laboratory. In fourteen months he began to lecture to a large audience.

But Watson at Cambridge was succeeded by Wollaston. We had to wait till Brodie for a successor to Boyle.

II.

We have seen what a vigorous effort Chemistry made to plant itself in Oxford in the seventeenth century. If the soil had been prepared the roots must have struck deep. But the University paid little heed, and after a few years of prodigal growth the plant withered and died out. It would seem that the positions are reversed at the present day. The University spends large sums for supervision and appliances: the young plants are brought here and nurtured at great expense, but the fair blossoms produce little fruit. Even our best friends admit that the results are somewhat disappointing, If these are the facts—and I speak as one who shares the responsibility for the present condition of chemistry here—it is the duty of those concerned to speak out; and I can conceive no more fitting opportunity than the present for pointing out some of the causes that appear to hinder our growth. Let no one think I wish to disparage the University. I should be the last person to do so. I owe to my old college the opportunity, the help, and the example which made me a chemist, and gave me an interest in life. I only wish to see more general the advantages it was my luck to meet with in Christ Church.

Chemistry in modern Oxford is accorded a place side by side with older studies. No one can complain that scholarships are not offered broadcast, that money has not been freely given for laboratories; and yet I think the student does not feel around him the atmosphere in which an experimental science should be cultivated. We see Chemistry endowed and extended, we do not see it respected by the bulk of students and of learned men. In my undergraduate days a rhyme was current here (I think it was coined in Cambridge—the Parnassus of parodies) expressing views which were undoubtedly held concerning the claims of chemistry as a subject for a degree. One verse ran—it was from the Lamentation of a would-be Bachelor—

> "I thought to pass some time before, but here, alas, I am,
> Having managed to be plucked in every classical exam.
> I cannot get up Plato, so my reverend tutor thinks
> I had better take up Chemistry, which is commonly called 'Stinks.'"

I do not quarrel with the versifier (except as a poet), I do not even quarrel with the reverend tutor, whose opinion of us is obviously small, because I do not think myself that Chemistry as it is taught is a very good subject for a degree. Still less is it a subject which we should allow to monopolise the schoolboy's time. While

holding strongly that the elements of Physics and Chemistry form a necessary part of a liberal education, I believe we have made two mistakes with regard to the teaching of science. We have by our science scholarships encouraged too early specialisation at school; we have overburdened our undergraduates here with a multitude of facts they cannot retain. A boy specialises for two years at school; he learns a prodigious array of facts from the latest text-book, and also acquires some skill in the art of quickly reproducing what he has learnt. He wins a science scholarship. We then tell him he must go back to, or begin, the study of the classical languages we look on as essential for our degrees. By a certain time he must reach a certain (rather low) standard, or his scholarship lapses. He learns that it is advisable to get assistance from those who have made a special study of preparing candidates for pass examinations. He crams; or he goes to a crammer and is crammed. Let us suppose, as is usually the case, that the obstacle is Greek. I will not deny that the standard of Greek demanded may imply some important discipline at school, and some real culture of the mind, provided the instruction given is on wholesome lines and forms part of a liberal course. Got up in a hurry as it too often is, solely with the object of passing, it means time and effort wasted and worse than wasted. It is of no value in itself, for it is forgotten in less time than it took to acquire; and it gives the student the first pernicious taste of that superficiality and false knowledge it should be our special aim to remove. Is it not desirable that scholarships should be the reward of progress and ability *in the general subjects of school education* among which the elements of science should have a place? The brightest and most persevering boys would come to the University, and there make choice of the special course they wished to pursue.

My second complaint is that we teach too many facts. They are not all important. After three or four years' steady accumulation our men go into the schools walking dictionaries of chemistry. Parents not unnaturally think that their sons, after four years of college training, should be fit to take responsible places wherever chemists are in demand. But manufacturers, as a rule, do not care for University graduates. I cannot blame them. We cannot guarantee that the men we send out with honours in Chemistry can attack a new problem, can work out new processes, can prepare new dyes. German manufacturers, on the other hand, *prefer* a University graduate, for they have in *their* degree a guarantee that the student has successfully attacked some unknown problem, and added to the store of knowledge.

The influence of science on the nation's industry has been recognised and insisted on by those who can make their voices heard. The country has at length awakened to the fact that something is wanting, and cries out for Technical Instruction. It is not afraid of spending money; indeed, many well-meaning bodies are spending—and in some cases, I fear, wasting—money with a prodigal hand. And what, after all, is the great need? Speaking for the subject I know best, I say unhesitatingly that we want scientific chemists who can and will make discoveries; we want men trained, not only in what has been done, but taught how to set about winning new knowledge. The Universities, I urge, should teach the art of research. This is what is wanted, and this, as all experience shows, is what the Universities can do better than anyone else. And no exorbitant amount of time need be demanded for this purpose. If the student has learnt the elements of science at school, three years at most should suffice for the preliminary degree course. The graduate, armed with the necessary manipulative skill, would then start research work under proper guidance as the second and more valuable portion of his University training. And here the new research degree (by whatever name it may be called) may give us most valuable help. I hope that serious work will be demanded for it, and that the research course will become the recognised avenue to science fellowships and lectureships in the University. Two years would show what the man had in him. In that time either he would have proved himself no chemist, or he would have made some useful advance in our knowledge, and would have secured a testimonial of fitness such as no examination could confer. Five years in all—the minimum time now laid down for a medical qualification—would surely be not too much to ask for the chemist's training.

No extra expense need be incurred to carry out this plan. Some of the college scholarships at present offered on entrance might be reserved for research studentships on graduation. These studentships should be the reward of the successful undergraduate career. On this point, which I have urged for many years, I am glad to find myself in entire agreement with the President of the Chemical Society. At Owens College our most successful endowment in Chemistry has been the Dalton Scholarship, awarded for a research done in the College laboratories. In the Victoria University we have lately founded scholarships for the encouragement of research, which are awarded on the results of the final examination in the several Honours Schools. The winners are entitled to hold their scholarships at any university at home or abroad where they can continue their special studies.

I plead, then, for greater encouragement of chemical research in Oxford. Make it part of the normal course of training for everyone who wishes to be a chemist in fact as well as in name. Consider, not only the country's need, but the value of research itself as a mental training, as stimulating and strengthening the activities, as creating that sense of devotion and discipleship which becomes the tradition of every great school of learning.

Lastly, let us own that we ourselves—the teachers here—have been perhaps too critical, too much afraid of making mistakes, forgetting that the witty American's remark, that he who never makes mistakes never makes anything, has a far wider application in science than in politics. Only by practice and drill can we learn to collect our strength and swing it with precision into acts. Without that training, no matter how much faculty of seeing a man has, "the step from knowing to doing" is rarely taken. There is nothing, I believe, in Oxford antagonistic to our cause. The genius of the place has not declared against scientific research; and if it be a true saying that men here imbibe a liberal education from the very air breathed by Locke and Berkeley, surely we also may draw scientific inspiration from this air, not only breathed, but first explained by Boyle and Hooke and Mayow.

THE ACTION OF CHLORINE ON PHOSPHONIUM IODIDE.

By J. C. CAIN, B.Sc. (Vict.), D.Sc. (Tübingen), F.C.S.,
1851 Exhibition Scholar in the Owens College, Manchester.

The action of chlorine on phosphine has been noticed by Thomson (*Ann. Phil.*, viii., 87), who states that when phosphine is led into chlorine it burns vividly with a greenish yellow flame, and a brown matter is deposited. He regarded this brown matter as a bichloride of phosphorus.

Leverrier (*Ann. de Chim. et de Phys.*, 1835, vol. lx., p. 174) states that when chlorine is passed into phosphine, phosphorus separates out; when the chlorine is mixed with an equal volume of carbon dioxide, the solid hydride of phosphorus, P_4H_2, is also formed.

It seemed to be of interest to try the action of chlorine on phosphonium iodide, as the experiment has not up to now been described.

When chlorine is allowed to act upon a few grms. of phosphonium iodide contained in a test-tube a vigorous action takes place. Hydrochloric acid is evolved, iodine

is separated and is volatilised by the heat of the reaction, iodine monochloride being also formed.

The substance becomes red, and on adding water this red substance is separated from excess of phosphonium iodide.

Some experiments were also made, using phosphorus pentachloride instead of chlorine. On mixing the two substances the red body is immediately formed, and it is likewise formed if the two substances are heated together in a sealed tube, or if the vapours of phosphonium iodide and phosphorus pentachloride are allowed to mix in an atmosphere of carbon dioxide.

This red substance is insoluble in water, and on being heated strongly in a current of carbon dioxide is volatilised. The substance condensed on the cool part of the tube was pure yellow phosphorus, and a gas was collected over potash which was found to be phosphine.

Thus the red substance was a mixture of the solid hydride of phosphorus with amorphous phosphorus, which is shown by the fact that the amount of phosphorus condensed was much greater than could have resulted from the decomposition of the amount of solid hydride corresponding to the volume of phosphine collected.

Thus the products of the action of chlorine on phosphonium iodide are free amorphous phosphorus and the solid hydride of phosphorus, *i.e.*, the same as those obtained by the action of chlorine, diluted with its own volume of carbon dioxide, on phosphine, though when pure chlorine reacts with phosphine, only ordinary yellow phosphorus (coloured red) is obtained, as Leverrier has shown.

The Owens College, Manchester.

THE MISSISSIPPI RIVER WATER.

By G. B. FRANKFORTER, M.A., Ph.D.,
University of Minnesota.

The water of the Mississippi river, coming directly from the beautiful crystal lakes of northern Minnesota, and flowing over the old Archæan rocks, one would naturally expect to be unusually free from impurities. Such, however, is not the case; on the contrary, the water contains so much organic matter, that here (at Minneapolis), where the maximum is evidently reached, the unusually large quantities seem important enough to record.

The peculiar properties of the water, and the fact that at several places it is used for potable purposes, led to a series of analyses, the only important results of which were the large quantities of free and albumenoid ammonia and organic matter. An average of several analyses above Minneapolis, and above where any large cities are situated, gave in the above-mentioned constituents the following results :—

Free ammonia	0·22	part per million.
Albumenoid ammonia	0·64	,, ,,
Organic matter (oxygen consumed)	22·	,, ,,

From inorganic matter and chlorine the water is exceptionally free.

Inasmuch as I have never known river water free from sewage to contain such remarkable quantities of ammonia and organic matter, I began to seek for a solution to the problem. An excursion up the river soon solved the problem.

During the spring and summer months millions and millions of logs are carried down by the current from the great northern forests to the mills here at St. Anthony Falls. The river from May to September is literally filled with logs, hundreds of thousands of which lie in the water one, two, and three years. A result is that the water becomes a decoction of bark and wood. Indeed, the residue, which is largely organic matter, contains tannates and gallates which are readily detected in the brown waxy mass.

THE SEPARATION OF THE RARE EARTHS.

By WILLIAM CROOKES, F.R.S.

An article appeared in last week's Chemical News (lxx., p. 68) on this subject from the pen of Professor Rowland, one of the most distinguished of American physicists. It is avowedly only a preliminary account, as we are promised a complete description of his work and results at a future time. A detailed notice of the paper must therefore be left till it is published in its entirety; but some of the statements in the preliminary notice deserve immediate comment.

It seems evident from internal evidence that the author of the paper has paid but little attention to the laborious and minute work done by the large number of chemists who have patiently toiled, month after month, and year after year, gradually separating one of these rare earths from another, and ascertaining their principal properties.* In the second paragraph the author, after noting that the earths of the cerium and yttrium groups appear in varying proportions in such minerals as gadolinite, samarskite, yttrialite, cerite, &c., goes on to say, "besides the elements of the cerium group, here present, there are at least seven other substances," which he speaks of as *a*, *b*, *i*, *d*, *h*, *n*, *c*, *k*. These, of course, belong to the yttrium group, but no notice is taken of many of the elements of this group now well known to chemists, and described long ago, such as (besides yttrium and erbium), holmium, thulium, terbium, scandium, ytterbium, dysprosium, and others which are not so well identified. This being so, why complicate matters by adopting new signs, instead of the now accepted names?

Substance *a* is said to be the principal element of yttrium. Does this mean that yttrium is considered to be a compound substance? It would appear not from the next paragraph, for there it is stated that "its oxalate and oxide are pure white and its properties are those of yttrium as hitherto obtained." Professor Rowland says that he is "the first to obtain it with any approach to purity." This is scarcely accurate, for pure white yttria, free from any known impurity, has been obtained in large and small quantities by many chemists years ago, and has been taken as the starting point in my private laboratory for some years past, for the separation of its meta-elements. The atomic weight of this yttria is 89. Has Professor Rowland taken the atomic weight of the yttrium which he calls *a*?

Further on the author says that a certain mixture of *b*, *i*, and *d* "seem to be the principal ingredients in so-called 'erbium,'" and that the oxalate is red, the oxide pure white, and the absorption-band is that of erbium. It is difficult to understand this. Erbia has an almost white oxalate, not red; its oxide is of a delicate rose colour, not white; its absorption-spectrum has many bands, and its

* In the Address to the Chemical Society delivered in the year 1889, I gave a list of the constituents of the rare earths known and definitely named at that date. The list included the following:—

	At. wt.
Neodymium	140·3
Praseodymium..	143·6
Decipium	—
Samarium	150·12
Lanthanum	138
Erbium	166
Philippium	45—48
Holmium	—
Thulium	170·7
Dysprosium	—
Yttrium	88·9
Terbium	124·7
Gadolinium	—
Ytterbium	173·01
Scandium	44·03

In the same paper I brought forward evidence to show that most of the above bodies were compound, and gave a list of fifteen new bodies into which I had separated them. At the same time I showed that there was a probability, according to Krüss and Nilson, that the number of constituents might rise to twenty-two or more.

atomic weight is 166. True, that from this old erbia other elements have been removed—holmia, thulia, and dysprosia—but its whitish oxalate and rose coloured oxide remain characteristic.

Recent researches show that even here we have not attained finality, but that this rose-coloured erbia can be split up into two or more others. Moreover my own experiments show the extreme probability of these two new constituents of erbia being compound. Now when we are told that some unknown and unnamed bodies, *b*, *i*, and *d*, are the principal ingredients of so-called erbium, chemists are entitled to ask Professor Rowland to define his "so-called erbia," and to say whether he means the mixture of holmia, thulia, dysprosia, erbia 1, erbia 2, and the several meta-elements into which many of these earths have been split up, whether he means any special mixture of some or all of these as found in a particular mineral, or whether he means only one of these bodies. Whichever way the "so-called erbia" is looked at the few properties given by the author will not fit. No information is given as to what is understood by the absorption-bands of erbium. The original erbium of Mosander, 50 years ago, had a definite and well-mapped absorption spectrum. And although from this body successive chemists have split off four or five separate elements, each having its own absorption-spectrum, the residual erbium retains a very respectable system of bands.

That a substance occurring in the yellow part of a sample of yttria (which if it is yttria should be pure white and not yellow) should be difficult to separate, is only what every chemist who has worked on these earths has long found out, but this difficulty is scarcely a reason for calling it a new element and giving it a demoniacal name. In a sample of yttria sufficiently impure to be of a yellow colour, many substances are present. These are extremely difficult to split up; nevertheless chemists have separated them, and have described their properties, ascertained their atomic weights, and have given them names which are accepted by other chemists.

In the name of exact chemistry I must protest against the principle of taking a heterogeneous mixture of substances, the separation of one from the other and the properties of which have occupied the utmost skill of well-known chemists all over the world for the last fifty years,—of taking this mixture and dividing it up into a few parts, less in number than its known constituents, and naming each arbitrary part afresh, culminating in the cacophonous word "demonium."

The varying solubility of the double sulphates in sulphate of potash or sulphate of soda is one of the earliest methods of separating the cerium and the yttrium groups. It would be difficult for any chemist to carry the minute examination of this method and its power of taking the constituents out one after the other to a higher degree of refinement than has Marignac, not to mention the many other chemists who have worked on this branch.

Ferrocyanide of potassium was used by Behrens in 1891, and my own experience with it has shown that it is little, if any, better in completeness than others of the now numerous methods of fractionation. Useful it certainly is, for any one method of fractionation will only separate up to a certain point. A balance seems to be struck after a little time, when the special method employed has exhausted its powers. Another method of fractionation must then be adopted, when the cleavage will take place along another line. By thus varying the method, and using each in turn on the products of a previous process, all the modes of cleavage can be made use of and the scission be extended to the fullest degree. For this reason any new process of partial separation is of value, but the ferrocyanide method is not new, neither is it in my hands, at all events, of such general applicability as would be supposed from a perusal of Professor Rowland's paper.

It is probable that when the full paper comes to be published the points here taken up will have been fully gone into, and the present remarks prove to be unnecessary. If this be the case no one will rejoice more than the writer. But on the paper now before the world it cannot be said that these comments are hyper-critical. Every man of science, whether he be chemist or physicist, is under a deep debt of gratitude to Professor Rowland for the magnificent maps of the solar spectrum he has placed at their service. In other ways also he has done good work, monumental work, in science. If his photographed spectra of the rare earths and their constituents bear out the statements in the preliminary note, he will have achieved a triumph in face of which his other great discoveries will take second rank. He will have entered the lists in competition with nearly all the great chemists of the past half century, and in a few short years, without using their accumulated knowledge (or surely the indebtedness would have been acknowledged), he will be in a position to solve problems in chemistry which, if not absolutely insoluble, have hrtherto been relegated to a position not very far from the border line separating the possible and impossible.

NOTES ON WATER ANALYSIS.

By C. A. SEYLER, B.Sc.
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I.

The interpretation of the results of water analysis has always been a subject of great dispute, and the recent progress of bacteriology has re-opened the whole subject, even to the extent of denying the hygienic value of chemical analysis (see Kruse, *Zeit. Hyg.*, 17, 1). A brief review of the chief fixed points established is therefore important. These relate (1) to the necessity of hygienic examination, (2) to the problem of water analysis, and (3) to the facts upon which judgment must be based, and may be summarised as follows:—

1. Natural water is in general a very dilute solution of certain salts, organic matter, and gases, holding in suspension traces of matter, largely living organisms.

2. These matters are generally, in themselves, of no hygienic importance unless they affect the appearance, taste, or smell (*e.g.*, iron salts, peaty matter, &c.).

3. Except in the case of a few metals specifically poisonous (such as lead) and organisms specifically pathogenic.

4. Certain pathogenic organisms (chiefly those of cholera and typhus, and possibly tubercle and anthrax) can survive for long periods in water, and the respective diseases have been proved conclusively to be often water-carried.

5. The chief vehicles of pathogenic organisms are fæcal matters and household waste-water (sewage).

6. Exposure to sunlight and oxygen, and competition with other organisms, are powerful purifying agents (as in running water).

7. Filtration, artificial or natural, removes micro-organisms very completely. The surprising efficacy of proper sand-filtration is well seen in the London waters, and in the experience of Hamburg and Altona during the last cholera outbreak (Koch, *Zeit. Hyg.*, xiv., 393). Natural filtration is even more efficient. Fraenkel and others have shown that ground-water is normally sterile, even when of polluted origin. There are, however, important exceptions, and the filtration, being chiefly due to the surface layer, may at any time fail or be entirely absent if the surface be of coarse gravel, or if the impurity originates at a depth, *e.g.*, by a leaking drain or cesspool. The conditions of efficacy are not under control (see Fraenkel, *Zeit. Hyg.*, vi.).

8. Upon these facts we may state the problem of water analysis to be, not the present condition only, but the permanent immunity of the supply from the entrance of

pathogenic organisms or their vehicle (and, of course, freedom from poisonous metals or liability to attack them).

9. A judgment on this involves a knowledge (1) of the nature of the source, (2) the subsequent history of the supply, if subjected to proper filtration, (3) the storage.

10. Thorough inspection of the supply is evidently the first condition of a sound judgment. It is, however, often very difficult to obtain, and very imperfectly supplied, or even purposely withheld. In the case of underground waters it must necessarily be incomplete.

11. Quantitative bacteriological methods have their chief and great value as a control of the efficacy of artificial filtration if the sample be properly taken and promptly examined. The estimation of oxidisable organic matter and of colour are also of particular service for this purpose.

As a control of natural filtration, bacteriology is of less use owing to the practical difficulties of sterilising the means of collection (tube or shaft of well) (see Fraenkel, *loc. cit.*). Moreover, it offers no guarantee of continued efficacy.

In the case of underground waters we are therefore thrown back upon chemical methods. The use of these depends on the following assumptions.

12. Natural waters may be classified into groups of fairly constant chemical characteristics—(*a*) upland surface from uncultivated ground; (*b*) mixed surface water (streams); (*c*) underground water, deep or shallow.

13. The vehicle of pathogenic germs (sewage, &c.) has fairly definite chemical characteristics (high organic matter, especially nitrogenous, ammonia, chlorine, &c.).

14. The characteristics of the vehicle are either maintained, if directly introduced, or altered by infiltration through soil in a definite way (oxidation and nitrification). Thus the presence of bodies like chlorine, ammonia, nitrates, in themselves harmless, may have great value as indicating the origin and past history of the water. The above assumptions are undoubtedly broadly justified by experience, but much room remains for a completer study of the chemical characteristics of the various classes of natural water and the chemical effects accompanying natural filtration. The subsequent notes are intended as a contribution to the methods of study mainly from the somewhat neglected side of the dissolved gases.

(To be continued.).

COMPARATIVE RESEARCHES ON THE PRODUCTS OF COMBUSTION OF COAL-GAS AS YIELDED BY AN ARGAND BURNER AND BY AN AUER BURNER.

By N. GREHANT.

I have submitted the products of combustion of coal-gas to new investigations, making use of the chemical procedure with copper oxide and of my chemical-physiological method, which enables me to determine the smallest traces of carbon monoxide with the utmost accuracy.

For the complete absorption of the carbonic acid I made use of three Cloëz bottles filled with a filtered solution of potassa in baryta water. We learn from a ring of barium carbonate the moment when the third bottle begins to absorb carbonic acid. The two first, being insignificant, are set aside. The gases then traverse two check-tubes containing baryta water of 0·70 metre in length, which should always remain perfectly clear. To the end of the combustion tube is attached another tube of baryta water. All the points at which the external air might enter are coated with caoutchouc muffs full of water.

Verification of the Apparatus.—I make in a gasometer constructed on the model of that of Dr. St. Martin a mixture of 34 litres of air and 3·4 c.c. of pure carbon monoxide—a mixture of 1 part in 10,000. I cause the gas to pass slowly bubble by bubble through the red copper oxide by means of a Galaz pump and a mercury pressure gauge. There appears a well-marked ring in the last baryta tube. The decomposition of the barium carbonate in the vacuum of the mercury pump gave 3·4 c.c. of carbonic acid, corresponding exactly to 3·4 c.c. of carbon monoxide.

Argand Burner.—I light an Argand burner enclosed in a chimney of glass and a metal lid communicating by means of a refrigerant and a long caoutchouc tube with the gasometer, in which there is effected a decrease of pressure of 2 c.m. of water; the products of combustion fill 150 litres in six minutes.

The gas is caused to pass gently over the copper oxide for twenty-four hours, obtaining, for 73 litres, a slight ring of barium carbonate, which when decomposed gives only 1·2 c.c. of carbonic acid. Hence, in the products of combustion of the Argand burner, there exists a trace of gas containing carbon, but the proportion is so slight that it may be estimated at $\frac{1}{72000}$.

On causing a dog to inhale the products of the combustion of an Argand burner (after having taken a specimen of normal blood in order to determine the combustible gas of the blood), I found that a second specimen of blood gave the same reduction, 0·91, which confirms the former result and demonstrates the absence of carbon monoxide in the products of combustion.

Auer Burner.—It is no longer the same on operating with the Auer burner, which gives so white and dazzling a light.

On passing 60 litres of the gas obtained from the combustion of this burner, I obtained, after the copper oxide, a bulky precipitate, which I submit to the Academy and which when decomposed in a similar experiment gave 23·2 c.c. of carbonic acid, corresponding to 23·2 c.c. of formene or carbon monoxide, or a mixture of both gases. The proportion of this gas in the products of combustion is $=\frac{1}{2586}$.

On examining with an animal if this gas contained carbon monoxide, I obtained a positive result. After respiration for half an hour I obtained 1·3 c.c. of carbon monoxide from 100 c.c. of blood, which represents in the air $\frac{1}{7200}$ of carbon monoxide. Hence from a sanitary point of view it is very important to allow the products of the combustion of coal-gas to escape into the open air, especially if derived from the Auer burner. — *Comptes Rendus*, cxix., p. 146.

NOTICES OF BOOKS.

Coal Dust, an Explosive Agent; as shown by an Examination of the Camerton Explosion. With Seven Plates. By Donald M. D. Stuart, F.G.S., Mining and Civil Engineer. London: Office of the *Colliery Manager* and E. and F. N. Spon. New York: Spon and Chamberlain. 1894.

The recent calamity in Wales has convinced the nation that all the conditions of such disasters are not yet fully recognised, much less provided against. For a long time it was supposed both by the public and by experts that coal-mine explosions were due simply to the gaseous hydrocarbon known to chemists as methane, but dreaded by miners under the name "fire-damp." It was hoped that by the invention of safety lamps and by the introduction of systematic ventilation this evil genius had been exorcised, and that the explosions which still happened were due to the perversity of the miners, who, in defiance of all precautions, still carry down matches into the mine.

But explosions were unfortunately found to occur in coal mines nearly or absolutely free from fire-damp. Hence some other cause must exist. That cause, ac-

cording to the experimental researches of Prof. W. Galloway, Prof. Freire Marreco, Mr. H. Hall, and other inquirers, is coal-dust. It is known that combustible substances generally, if finely pulverised, and suspended in air, burn violently and even explosively. In the gigantic grain mills of Minnesota serious explosions have been occasioned by flour suspended in air and being ignited. Coal-dust cannot fail to act in a similar manner, and it has been substantially proved that in fire-damp explosions coal-dust is in many cases an important accessory. Messrs. H. Hall and W. Galloway went further and suggested that air charged with coal-dust may produce all the phenomena witnessed in mine explosions in the total absence of methane. The views of Hall and Galloway were received with scepticism as being not in accord with general experience. It was contended that the dust from non-gaseous mines was non-explosive and harmless, and that consequently the coal-dust theory was applicable only in presence of methane. Prof. Bedson showed experimentally that coal dusts varied in inflammability when mixed with air. Here Mr. Stuart comes in and clears up the difficulty, showing how and under what conditions coal-dust is capable of becoming explosive. The key was afforded him by an explosion which took place in November last at the Camerton Collieries, Somersetshire. These mines were absolutely non-gaseous, so that, like other mines in the same seams, they have been, and still are, worked with candles or other naked lights. Everything was proceeding normally when one evening, after the ordinary work was over, two men were told off to blast the roof of an incline which had sagged down, so as to obtain sufficient height for the loaded trucks to pass. They had bored and fired one hole and cleared away the matter dislodged, and proceeded to bore and fire a second hole. It appears that this second shot was, as it is called, "blown out." The energy liberated on the explosion of the powder, instead of expending itself in the fracture of the rock, was thrown upon the coal-dust on the ground, which was thus submitted to destructive distillation. The gases liberated, hydrogen and hydrocarbons, must have been ignited at the moment of their formation. The result was not a single explosion pervading the mine, as in the case of fire-damp, but a series of ten discontinuous explosions, extending together over a length of more than 1000 yards, the gases being re-generated as long as coal-dust was present and a sufficient supply of atmospheric air was at hand. There must have been a constant production of explosive gases which could not be ignited because the supply of oxygen was insufficient. But as soon as these gases reached a space in the workings where there was a sufficient supply of air explosion ensued.

On a careful perusal of Mr. Stuart's book we are convinced that he interprets the phenomena in strict accord with the facts observed and with well-known chemical and physical laws. Coal-dust undergoing continuous distillation in the way described, and liberating combustible gases, is the only agent which can have come into play. That the dust thus acted on is proved by the residues left in sheltered places which have evidently been *coked*. That the explosion was intermittent and not continuous is proved by the alternation of damage with portions of the workings uninjured, the wreckage being at or near the points where the gases evolved could not meet with a supply of oxygen.

Very great value must be allowed to the precaution urged by Mr. Stuart, viz., the saturation with water of all coal-dust near the spot where a shot is to be fired. Mere moistening or damping is insufficient, since the moisture might be evaporated away by the heat generated by a "blown out" shot, or by one in which an excess of gunpowder has been used. It will be remarked that the more thorough the ventilation the more quickly coal-dust which is simply damp will be dried.

Mr. Stuart has fully demonstrated that the dust even from non-gaseous mines is dangerous, and under what circumstances this potential danger becomes real. He has shown a certain and inexpensive precaution—which, we hold, ought to be made legally compulsory—and he has thus conferred a great benefit not merely on the coal-owner and the working miner, but on the nation at large.

Science Progress; A Monthly Review of Current Scientific Investigation. London: The Scientific Press, Limited. July, 1894.

In the current number of this journal we note an innovation which will be of considerable value to many readers. It is an enumeration of the titles of chemical papers appearing in May, 1894, in all the best known English and foreign journals. It is intended to continue this list for each month, and if done thoroughly it will save a good deal of time for those wishing to read up any particular subject.

Victoria University. Yorkshire College, Leeds. Report of the Work of the Textile Industries, Dyeing and Art Classes, and the Leather Industries Department for the Session 1893-94.

We note that during the current session there have been improvements in machinery, extensions of class work, and several new elements introduced into the year's activities. The Senior Classes are steadily growing, while at the same time the standard of excellence in the Junior division is higher than it has been in any previous year. A publication called the *Textile Students' Magazine* has been started by the students, and the idea being taken up with enthusiasm, the undertaking has been a success both financially and otherwise.

In the Dyeing Department the number of students and their general attendance has been very satisfactory, and the results of several researches carried on in the department have been published in the *Transactions of the Chemical Society*. The same continued improvement is to be noticed in the Leather Industries Department, and attention is drawn to the fact that Messrs. W. Beckworth and Son have allowed the use of their tannery for practical illustration and experiments. This permission has been found to be most valuable to the students, who have gladly availed themselves of it.

Imperial University. College of Agriculture. Bulletin Vol. II., No. I., May, 1894. Tokyo, Komaba: Printed by Hakubunsha. Giuga, Tokyo.

This Bulletin contains two papers; the first is by Dr. Oscar Loew, on "The Energy of the Living Protoplasm." It is divided into four chapters. Dr. Loew begins by reviewing former ideas on the cause of the vital phenomena, and draws attention in a forcible manner to the wonderful and mysterious change from life to death. The death of the lowest forms of animal or vegetable life as viewed under the microscope is as striking as the death of the largest animal or plant; the motions of infusoria cease, the diatoms stop, their nucleus leaves its normal position. All energy, mechanical or chemical, is gone. The attempts to penetrate these mysteries in a truly scientific manner are of comparatively recent date, and the author, after summing up the opinions of many workers and writers, concludes that there is a *chemical* difference between living and dead protoplasm. Hanstein defined protoplasm "as a semi-liquid substance consisting of proteids insoluble in water, generally of neutral reaction, transparent, and refracting the light a little more than water." But this definition is not perfect; we miss the chemical side of the question, above all the distinction between living and dead protoplasm. In 1875 Pflüger treated this problem scientifically; he started from the chemical fact that living cells take up oxygen, while the dead ones do not. From this fundamental difference he argues that living protoplasm is exceedingly liable to chemical change, and if that change takes place death results.

Alumni Report. Published by the Alumni Association of the Philadelphia College of Pharmacy.

We have received Nos. 7, 8, and 9 of this journal. It is, as its name indicates, the official journal of the College, and contains a good deal of information concerning the current events in and connected with that Institute. It has also a few columns devoted to personal news and to general items of scientific interest.

MISCELLANEOUS.

British Association for the Advancement of Science.—The following are the names of the Officers and Committee of Section B (Chemical Science) of the Oxford Meeting of the British Association :—

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The Papers brought before the Section were as follows :—

President's Address.

Report of the Committee on an International Standard for the Analysis of Iron and Steel.

Report of the Committee on Electrolytic Methods of Quantitative Analysis.

Prof. F. Clowes—On the Proportions of Carbonic Acid in the Air which are Extinctive of Flame, and which are Irrespirable.

Dr. Lobra de Bruyn—Some Experiments on Free Hydroxylamine.

Dr. Alexander Bernstein—The Chemical Action of a New Bacterium in Milk.

Discussion on the Behaviour of Gases with regard to their Electrification and the Influence of Moisture on their Combination.

Prof. J. J. Thomson, F.R.S., showed Experiments illustrating the Connexion between Chemical Change and Electric Discharge through Gases.

H. Brereton Baker showed Experiments on the Influence of Moisture on the Combination of Chemical Substances.

Dr. Thomas Ewan—The Rate of Oxidation of Phosphorus, Sulphur, and Aldehyd. (Discussion followed).

Prof. W. N. Hartley, F.R.S.—New Methods of Spectrum Analysis and on Bessemer Flame Spectra.

J. W. Thomas—On the Chemistry of Coal Formation.

Dr. S. Rideal—Iodine Value of Sun-light in the High Alps.

Report of the Committee on the Formation of Haloids from Pure Materials.

Report of the Committee on the Bibliography of Solutions.

At a Joint Meeting of Sections A and B, Lord Rayleigh and Prof. Ramsay gave a preliminary account of a New Gaseous Constituent of Air.

Prof. H. McLeod, F.R.S.—Schuler's Yellow Modification of Arsenic.

Prof. Roberts-Austen, F.R.S.—The Electrolysis of Glass.

Prof. T. E. Thorpe, F.R.S., and J. W. Rodger—The Relations between the Viscosity of Liquids and their Chemical Nature.

Dr. J. H. Gladstone, F.R.S.—Some Experiments on the Rate of Progress of Chemical Change.

P. B. Lewis—Method of Determining the Freezing-point in very Dilute Solutions.

Dr. M. Wildermann—The Freezing-point of Water.

Dr. W. W. Randall—On Apparatus to Measure the Effect of Dilution on the Colour of Salt Solutions.

P. J. Hartog—Distinction between Compounds and Mixtures.

J. A. Wanklyn—New Evidence as to the Atomic Weight of Carbon.

Dr. J. B. Cohen—Approximate Method of Estimating Carbon Dioxide in Air.

A. P. Laurie—On the Diffusion of very Dilute Solutions of Chlorine and Iodine.

Prof. J. W. Brühl—Investigations on Tautomerism.

Prof. E. Noelting—On Dinitroso-Derivatives of the Aromatic Series.

Prof. E. Noelting—On the Formation of Indazoles from Diazo-compounds.

Dr. H. Caro—On some New Colouring Matters.

Drs. G. G. Henderson and A. R. Ewing—Tartrarsenites.

Dr. J. B. Cohen—The Constitution of Acid Amides.

Prof. W. R. Hodgkinson and A. H. Coote—Fluorene Diacetate.

Report of the Committee on the Bibliography of Spectroscopy.

Prof. J. J. Hummel—Report of the Committee on the Action of Light on Dyed Colours.

Prof. H. E. Armstrong, F.R.S.—Report of the Committee on Isomeric Naphthalene Derivatives.

Dr. W. Meyerhoffer—On certain Phenomena of Equilibrium during the Evaporation of Salt Solutions.

J. E. Marsh and J. A. Gardner—Some Derivatives of Camphene.

Prof. P. P. Bedson—Report of the Committee to Inquire into the Proximate Chemical Constituents of the various kinds of Coal.

Dr. W. W. J. Nicol—Report of the Committee on the Properties of Solutions.

Dr. Marshall Watts—Report of the Committee for Preparing a New Series of Wave Length Tables of the Spectra of the Elements.

Dr. W. H. Ince—The Preparation of Adipic Acid by Oxidation of Sebacic Acid and of Fats.

Dr. W. H. Ince—Note on Phenyl Acetic Aldehyd.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

The Herapathite Test.—I was much interested in reading M. Carey Lea's article on "Relative Affinities of Acids" (Chem. News, lxx., p. 55), but not having access to any Library or other means of perusing the *Am. Chem. Journ.*, I was at a loss to understand the "herapathite test" for free sulphuric acid which is the key to his paper. Could you oblige me and others by giving this test in your paper (which has been my constant pleasure for years past) either in the "Notes" or text?—W. R.

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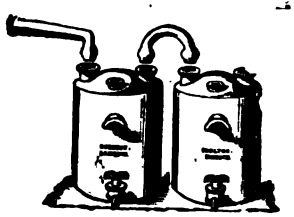

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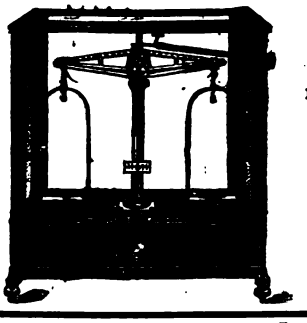

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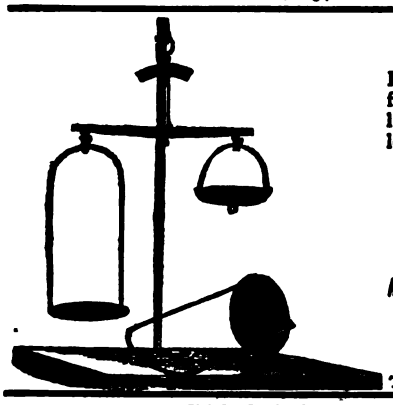

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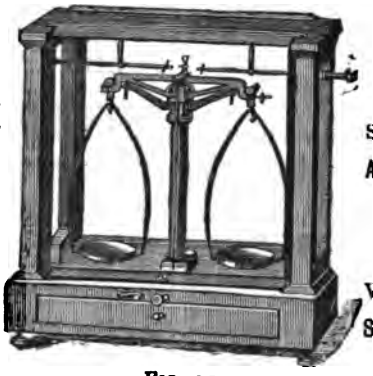

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THE CHEMICAL NEWS.

VOL. LXX., No. 1813.

A SUPPOSED NEW GASEOUS ELEMENT IN THE ATMOSPHERE.

CONSIDERABLE interest was excited in the Chemical Section of the British Association at the recent meeting at Oxford by the statement by Lord Rayleigh and Professor Ramsay that they had detected and isolated a new gas, supposed to be elementary, in the atmosphere. Some time ago Lord Rayleigh announced to the Royal Society that some anomalies in the densities of samples of nitrogen from different sources had led him to the conclusion that atmospheric nitrogen, carefully purified from every other known constituent of the air, was contaminated to the extent of about 1 per cent with another gas, even more inert than nitrogen. Since that time Lord Rayleigh and Professor Ramsay have been working in the endeavour to isolate the gas and determine its principal properties.

Two methods of preparing the gas have been devised. The first is to pass a series of high tension electric sparks through a mixture of air and oxygen (approximately equal bulks) confined in a eudiometer vessel over dilute caustic potash. The nitrogen and oxygen unite, forming nitrous and hyponitric acids, &c., which are absorbed by the potash, and if the sparking is long enough continued, and the oxygen is kept in slight excess, after a few hours a residue is obtained which suffers no further diminution in bulk by further passage of sparks. This residue is then purified from excess of oxygen by alkaline pyrogallate.

The second method of preparing the gas consists in passing air first over metallic copper at a red heat to remove the oxygen, and then passing the nitrogen over heated magnesium. The magnesium unites with the nitrogen to form a nitride, and the new gas is left behind. It may be advisable to get rid of the last trace of nitrogen by sparking with oxygen over potash, as in the first process.

Inertness seems to be the chief characteristic of the new gas. Its density is 18·9, if allowance is made for solubility in water, or 20· if no allowance is made.

Through the kindness of Professor Ramsay the writer has been enabled to photograph and examine the spectrum of the gas, when the induction spark is passed through a tube containing it under an exhaustion of about 8 millims., and to compare it with that of nitrogen under similar circumstances.

The spectrum is a very definite and characteristic one, and the lines differ in position from those of nitrogen. The appearance more resembles a metallic spectrum, and no flutings similar to those of nitrogen are to be seen.

The following letters from Professor Dewar on this subject have appeared in the *Times* for the 16th and 18th inst.

THE NEW ELEMENT.

To the Editor of the Times.

Sir,—In your report of the important paper communicated by Lord Rayleigh to the British Association, on a new gaseous constituent of the atmosphere, no mention is made of the evidence of the existence of such a body drawn from well-known phenomena occurring during the liquefaction of air. If a vessel be cooled to the temperature of 200° below zero Centigrade it quickly fills with liquid air, and every gaseous substance, elemental or compound, at present known, amounting to anything like 1 per cent, and boiling at a temperature above −200°, must become liquid or solid under such conditions. Thus when air is liquefied it does not appear as a clear transparent substance, but as a fluid containing more or less of a white deposit, due to the solidification of carbonic acid and other gaseous impurities, which floats in the transparent liquid oxygen and nitrogen. When air under high compression is used to produce the liquid in quantity, then, however carefully it may be purified before compression, it always takes up traces of foreign substances in its passage through the compressors, so that the amount of white solid associated with the liquid air may vary considerably, but is always present in greater or less quantity.

When I have been asked, during the last year or two, What is the nature of the solid, in so far as it does not consist of known atmospheric impurities? my answer has always been that I could not say, not having made a special study of the substance. Can this substance, which has been so often seen in the theatre of the Royal Institution, be in the main anything else than Rayleigh's new nitrogen in the solid form? If a hitherto unrecognised substance, elemental or compound, exists in air, having a density of about 19, and present to the extent of even a minute fraction of 1 per cent, chemists would infer that the material must be less volatile than nitrogen or oxygen, and therefore must be condensed with them in the process of liquefaction. Further, as the nitrogen of liquid air boils off first, leaving the oxygen with its higher boiling-point behind, so the new substance ought to remain liquid or solid after both these substances have distilled off. If the white solid (known impurities of course excepted) be not the new gas of Rayleigh, then the gas must liquefy along with the nitrogen and oxygen, and be approximately equal in volatility with one or the other. Then, on the other hand, the white substance certainly does not amount to 1 per cent of the liquid, and whenever I have casually examined it the substance has turned out to be a mixture of nitrous oxide, carbonic acid, and some other impurity. Therefore the amount of any unknown substance must necessarily be extremely small. One is forced to the conclusion that if the new nitrogen is present to the extent of ½ to 1 per cent, and has a density of about 19, then it is, indeed, a strange substance, being as volatile as nitrogen or oxygen, and therefore not capable of separation by difference of boiling-point.

These facts in no way detract from the interest of Lord Rayleigh's discovery; they only add some additional interest to the subject, and may suggest some queries to be answered by further investigation.—I am, Sir, your obedient servant,

JAMES DEWAR.

Royal Institution, Aug. 15.

THE NEW ELEMENT.

To the Editor of the Times.

Sir,—In my letter of yesterday I pointed out certain difficulties which suggest themselves as to the elementary character of the new constituent of the atmosphere, and its presence in normal air to anything like the amount of 1 per cent. If, however, we assume the substance separated by Lord Rayleigh and Professor Ramsay to be composed of known elements, then the experimental results can be easily explained. We have only to assume that when nitrogen enters into chemical combination with another substance, whether oxygen, as in the case of Lord Rayleigh's plan of working, or magnesium, as in that of Professor Ramsay, a small portion of the gas is condensed molecularly into an allotropic form, having 1½ times its normal density. We are familiar with such action in the case of the transition of oxygen into ozone, and practically identical methods are being employed in the assumed separation of the new substance from air. It would appear that electrical discharges acting alone

upon nitrogen do not condense it, and in this respect it differs from oxygen. Yet it is well known that electrical stimulation of nitrogen does produce two distinct spectra presumably due to different molecular conditions.

The theoretical density of the new nitrogen compared to hydrogen should be 21, while the experimental numbers are between 19 and 20, though these are admittedly too low. Such a body chemists would infer ought to be characterised by great inertness, because phosphorus, the element most nearly allied to nitrogen, easily passes into an allotropic form known as red phosphorus, which is relatively to the yellow phosphorus an inert body. If therefore such an active substance as phosphorus becomes in its condensed form far less active chemically, then by analogy nitrogen, so inert to start with, must in its new form become exceedingly inactive. No doubt the passage of the ordinary nitrogen or the diatomic form of the substance, to the triatomic form of the same, takes place with evolution of heat, just as in the similar transition in the case of phosphorus. While this hypothesis accords with the facts, it does not necessarily support the view that the triatomic nitrogen is present to the extent of one half per cent in normal air. On the contrary, the inference is that the new substance is being manufactured by the respective experimenters, and not separated, as they imagine, from the ordinary air. If the suggested view is correct it is certain that the allotropic nitrogen would be far less volatile than the ordinary variety, just as the vapour-pressure of red phosphorus is small as compared with that of the yellow, and, therefore, it ought to be separated from liquid air by its higher boiling-point, even if it did not become solid at the existing temperature. Its non-appearance supports the view that it can be present in air, if present at all, only in exceedingly small amount. Yet were it produced in ever such small quantity—for example, by the passage of electric discharges—its very inertness would favour its accumulation, just as the high chemical activity of ozone tends to its dissipation. If, therefore, in the long course of ages the quantity of this triatomic form of nitrogen remains inappreciable, we are scarcely entitled to assume its existence as a normal constituent of the atmosphere, unless we also assume that it is being utilised in some unknown way.

It is not the first time that chemists and physicists have been tempted to believe in the production of an allotropic form of nitrogen, and to accept it as explaining certain curious phenomena, but hitherto the assumption has always broken down on more careful investigation. This time we may be permitted to hope that the elusive allotropic form has been fairly captured.—I am, Sir, your obedient servant,

James Dewar.

Royal Institution, Aug. 16.

NEW EVIDENCE AS TO THE ATOMIC WEIGHT OF CARBON.*

By J. A. WANKLYN.

Members of this Section (who, like myself, a third of a century ago, were at that time charged with the responsibility of teaching Chemistry to the students of a University) will have a lively recollection of the incidents attendant on the change of notation at that period. The controversies of that day evolved, as will be remembered, a short and easy method of arriving at the molecular weight of a chemical substance, and likewise a short and easy method of finding the atomic weight of an element.

In Kekulé's words, very slightly modified, these methods were as follows:—

"Defining *standard volume* (or, as it was called, the standard two volumes) as *that volume* which is occupied by *two grms.* of *hydrogen* at a given suitable temperature and pressure, we were told that if we would know the molecular weight of any chemical substance we must ascertain how many grms. of the substance were required to fill the standard volume with the vapour of the substance, and that that number was the molecular weight. And the atomic weight of an element was to be found by observing what was the very least quantity of that element ever entering into the standard volume filled with a compound of that element."

Having laid down the law much in that style, advocates of the new notation forthwith proceeded to make the practical application by noting that the least number of grms. of carbon ever occurring in the standard volume of any carbon compound was 12—*ergo* the atomic weight of carbon is 12.

It was at the same time incidentally noted that in all those cases where more than 12 grms. of carbon was found in the standard volume, the number was either 24 or 36, or some other multiple of 12. And so the matter has rested until the present day.

I have now to announce that as the result of most laborious investigation, carried on conjointly with my friend and colleague Mr. Cooper, there exists a multitude of carbon compounds wherein the quantity of carbon in the standard volume is not a multiple of 12, but is a multiple of 6. And the consequence follows that the atomic weight of carbon is 6, as was commonly believed by chemists a third of a century ago.

Here is one of these carbon compounds which we have labelled Aa; its formula is $C_{7\frac{1}{2}}H_{15}$, writing the notation in vogue at the present day. We have six other half-carbon substances, viz., $C_{8\frac{1}{2}}H_{17}$; $C_{9\frac{1}{2}}H_{19}$; $C_{10\frac{1}{2}}H_{21}$ $C_{11\frac{1}{2}}H_{23}$; $C_{12\frac{1}{2}}H_{25}$; $C_{13\frac{1}{2}}H_{27}$.

The following are the vapour-densities as found and as required by theory:—

Found.	Theory.
3·69	3·63
4·08	4·11
4·59	4·59
5·02	5·08
5·51	5·56
6·08	6·04
6·53	6·52

These hydrocarbons exist in the Russian kerosene of commerce, from which they have been extracted by laborious and methodical fractional distillation. Further particulars of the investigation, which has occupied nearly two years, are to be read in the *Philosophical Magazine* for the month of May last, to which reference may be made.

The President (Professor H. B. Dixon)—Have you got any evidence besides these figures of weight and this liquid?

Mr. Wanklyn—None whatever. The liquid is a collection of similar chemical units. It is on such evidence that ninety-nine out of every hundred organic compounds stand.

Professor Odling—The subject brought before us by Mr. Wanklyn revives rather an old controversy. At the same time it is a subject of present as well as of historic interest. The atomic weight of carbon was fixed in the first instance by Dalton, and for nearly fifty years after Dalton's death. Although here and there it had been called in question by stray chemists, substantially all were agreed that in relation to the atomic weight of hydrogen taken as one, the atomic weight of carbon was six, Dalton was not by any means so sure of this; he recognised distinctly the evidence on which the selection of six, rather than three, or nine, or twelve being the atomic weight of carbon was not of a very definite character, and his selection of the atomic weight at six

* A Paper read before the British Association, Oxford Meeting, Section B.

was rather due to accident. He regarded olefiant gas as being a combination of one atom of carbon and one of hydrogen; and, supposing that to be the case, it is quite clear that the atomic weight of carbon would be six. About forty or fifty years after Dalton had enunciated the atomic theory, we were able, in the then comparatively advanced stage of organic chemistry, to form some determinations of atomic weights of bodies as distinguished from combining proportions on questions of fact, and more particularly on questions of the constitution and metamorphosis of a great number of organic bodies, and it was a result of this that the atomic weight of carbon was fixed at 12. The position I would venture to ask the Section to consider is this, that in fixing, in the first instance, the atomic weight at six, it was avowedly a mere shot. It was true it was a shot by a man of genius, and sometimes these stray shots of men of genius had a sort of prescience to recommend them, and proved to have some relation to what ultimately proved to be the case. It would require some consideration to induce us once more to return to the atomic weight of carbon as six. The determination as twelve is based on such a mass of converging evidence that it would require a very great deal to upset it. It comes to this, that until the observations of Mr. Wanklyn there were no facts, or apparent facts, that were seemingly in antagonism to that view, and that there was an enormous number of facts which led directly to it, and which, in fact, established that view, with such a weighty preponderance of evidence in favour of it. I quite recognise that up to the present time there is no group of facts antagonistic to Mr. Wanklyn's view; at the same time if a group of well-established facts were made out—even if a small group—it would be evident that we should have to make a change in our conclusions; and I would say further, that if any one fact could be made out that was in absolute antagonism, we should have to give up our present view. But the difficulty is to establish a single fact. What is the sort of fact we have before us? It is the question of boiling-point and vapour-density. Although Mr. Wanklyn did not make the observation, and although in a great many definitions the limitation is not made in words, it is to be understood we are dealing with a vapour which is a definite compound, and not with a vapour of the character which has been referred to a few minutes ago by Mr. Hartog in his address on the distinction between compounds and mixtures. In order to arrive at a conclusion of such importance, we must have a great deal more than the boiling-point and vapour density. We know that a great number of vapours are mixtures of closely allied bodies, and that the boiling-points may be for a long while perfectly invariable, and nevertheless not be the boiling-points of one substance, but the boiling-point of a mixture of several substances. As I understand, this body in the bottle before us contains of $7\frac{1}{2}$ atoms of carbon, or 15 atoms to the value of 6. If Mr. Wanklyn had from this produced a chloride in which one-fifteenth of hydrogen had been replaced by chlorine, and if from that he had got the alcohol and the aldehyd acid, &c., and made out the metamorphic relations of these compounds, it would have been very different. But it seems almost preposterous for one to give up such well-established conclusions on such very slender evidence; the evidence must be much more strong in order to convince chemists that the body before us is constituted of $7\frac{1}{2}$ atoms or 15 reduced atoms of carbon.

Prof. Friedel having addressed the Section in French,

The President said I think it is a late hour in the afternoon for me to invite any long discussion. I think the Section will agree with the weighty words which have fallen from Prof. Odling and Prof. Friedel, and we shall, I think, have to stick to the accustomed weight of carbon at 12, in spite of this clear liquid which Mr. Wanklyn has put on the table. At the same time I think our thanks are due to Mr. Wanklyn for what I may call his pluck in coming forward and presenting evidence of this kind. (Hear, hear). For myself, I think with Prof. Friedel that it is possible we may be too habituated to think of carbon as 12, and perhaps harden our hearts against any new discovery which may come before us indicating a new atomic weight. I hope, therefore, we shall pass a vote of thanks to Mr. Wanklyn for his communication. (Applause).

Mr. Wanklyn—The condemnation which I have heard pronounced is exactly what I expected. I thought I should be asked why I did not make a chlorine compound and go through the set. My reason is this. There is a parallel investigation with this of mine, which is very well known, and it is a very old investigation and a very celebrated one. It is the investigation by Cahours and Pelouze on American petroleum. The obtaining of the chlorine derivatives, &c., showed that the hydrocarbons were members of the marsh gas family, but did not go far to settle the other question. With great deference to Dr. Odling, I must say that the whole question resolves into this, Is my fractionation a successful one? does this liquid really consist of an immense multitude of molecules of the same kind, or does it consist of two or three multitudes of molecules of different kinds? I have worked for years on fractional distillation, and in 1861 I worked simultaneously with Berthelot, and we brought out one of the fundamental facts of fractional distillation. Two or three years later I brought out another fundamental fact of fractional distillation. I was very much amused at the criticism to which I was subjected. It was simply—It is perfectly true, but everybody knows it. But no one has acted upon it, but I have acted on the fact and have been able to carry out my fractionation, and my seven substances consist each of them of one single multitude of molecules, and not of several multitudes. I hold that the existence of these liquids establishes the smaller atomic weight of carbon. I have to remark this. There is a little confusion in saying there is much evidence against my view; there is no evidence whatever against it. That the atomic weight of carbon is 6 is not opposed to any known fact, and the recognition of the true atomic weight of carbon will bring into view a region of organic chemistry which up to the present time has been hidden from our sight.

Professor Ramsay suggested that Mr. Wanklyn should communicate with Dr. Young to corroborate his results.

Mr. Wanklyn said that he had the command of large quantities of the raw material which was the subject of the investigation, and that there would be many litres of the different liquids, and that chemists would be challenged to show that they were substantially impure.

Additional Note.—In my reply to Dr. Odling in the Chemical Section last Monday, I made mention that there were no known facts inconsistent with the value 6 for the atomic weight of carbon. According to my view, carbon has an atomic weight of 6, and is *triatomic*. This theory not only embraces all the compounds which are conformable with the ordinary theory at present in vogue, but it takes in the case of carbonic oxide, which cannot be explained by chemists who write carbon with an atomicity of 4 and an atomic weight 12.

According to my view this body is quite regular, viz.,—

which is the analogue of nitrous oxide—

The question why CH_3 is unknown I answer by saying that the inveterate tendency of carbon to unite with itself is the obstacle which stands in the way of the formation of the simplest carbon compounds.—J. A. Wanklyn.

ON THE DISTINCTION BETWEEN MIXTURES AND COMPOUNDS.*

By P. J. HARTOG, B.Sc.

The text-books attempt to distinguish between compounds and mixtures by stating that "the same compound always contains the same elements united in the same proportions," and imply that this is not true of the same homogeneous mixtures. But the statement interpreted literally is a truism, and not a law, and applies equally to both mixtures and compounds. Moreover, the statement has nothing to do with the Berthollet-Proust controversy, although it is supposed to sum up Proust's views on the matter. The theoretical distinction between compounds and mixtures was briefly discussed, and it was pointed out that the best experimental criterion for the purity of a chemical compound was afforded by the researches of Raoult, who has shown that any admixture invariably lowers its freezing-point and raises its boiling-point.

(For a fuller account of some of the points raised see *Nature*, June 14, 1894).

ON THE RATE OF OXIDATION OF PHOSPHORUS, SULPHUR, AND ALDEHYD.*

By THOS. EWAN, B.Sc., Ph.D.

Oxygen gas sometimes seems to show greater chemical activity when dilute than when more concentrated. At the suggestion of Professor van 't Hoff, the author studied the velocity of the reaction between oxygen gas and various substances which undergo slow combustion.

With phosphorus and oxygen (saturated with aqueous vapour at 20°) it was observed that no reaction took place when the pressure of the oxygen was greater than about 700 m.m. As the pressure falls, the velocity of the reaction at first rapidly increases, then remains approximately constant, and finally decreases. The reaction takes place in all probability between phosphorus vapour and oxygen. The quantity of phosphorus vapour present depends on the velocity with which the phosphorus evaporates, and this velocity increases as the pressure of the oxygen diminishes.

When this change in the velocity of evaporation of the phosphorus is allowed for (by a formula due to Stefan), the velocity of the reaction is found to be proportional to the pressure of the oxygen up to a pressure of between 500 and 600 m.m.

When dried oxygen is used instead of oxygen saturated with aqueous vapour, the reaction first begins at a much lower pressure (about 200 m.m. at 20° C.). After allowing, as before, for the change in the rate of evaporation of the phosphorus, the velocity of the oxidation quickly increases to a maximum as the pressure falls, and then decreases proportionally to the square root of the pressure of the oxygen. The course of the reaction was, however, somewhat irregular, owing, probably, to the formation of a layer of oxide on the surface of the phosphorus.

The connection between the rate of oxidation and the pressure of the oxygen could, however, be made out with certainty when sulphur was used in place of phosphorus. The reaction takes place with convenient speed at 160°. It was found that between pressures of 40 and 800 m.m. (beyond which limits no measurements were made) the velocity of the reaction is proportional to the square root of the pressure of the oxygen. The change in the rate of evaporation was also in this case taken into account.

Some uncertainty attaches to these results owing to the correction for the change in the rate of evaporation.

The reaction between aldehyd vapour and oxygen was therefore studied, whereby this uncertainty is eliminated. It was found that at 20° and in the dark, the reaction goes with perfect regularity, acetic acid being formed. Its velocity was proportional to the product of the pressure of the aldehyd vapour and of the square root of the pressure of the oxygen, up to pressures of the oxygen of about 450 m.m. These facts point to the conclusion that in these processes of oxidation only that small portion of the oxygen which is dissociated into atoms takes part in the oxidation—a result which is in accordance with the theory of the mechanism of a chemical reaction due to A. W. Williamson.

ON THE IODINE VALUE OF SUNLIGHT IN THE HIGH ALPS.*

By Dr. S. RIDEAL.

At the meeting of the Association in Nottingham I had an opportunity of submitting the values of the sunlight in the Upper Engadine in terms of the amount of iodine liberated from an acidulated solution of potassium iodide during the month of January, 1893. These experiments have been continued during the months of January and February of the present year by my brother, A. W. Rideal, and the results may therefore not be without interest. The recent experiments were conducted in exactly the same way as those of last year, so that in all respects they are strictly comparable. The solutions were standardised by standard iodine solution prepared in England, and the hyposulphite solution was checked against this solution from time to time during the progress of the experiments.

During the last winter the weather was on the whole bad, and the number of days on which snow fell or which were overcast were more numerous than in the corresponding period of last year.

The maximum value was obtained on February 4th, and was equal to 14·52 m.grms. of iodine per 100 c.c., as compared with 13·5, the maximum value on Jan. 1st, 1893. The lowest value was 3·53 on December 9th, 1893, as against 5·7 on Jan. 24th of last season. The number of bad days on which little or no sun was recorded lowers the average for the period under examination. It amounts to 7·05 m.grms. per hour, whilst in Jan., 1893, taking only the bright days, the quantity was 9·34.

I understand that the ordinary meteorological record was kept as usual, and that the data are to be found in the *Alpine Post* for the days on which these experiments were carried out. I append, however, a brief note as to the atmospheric conditions in a separate column.

Date,	No. of hours.	Total m.grms. Iodine per 100 c.c.	Hour value.	Conditions.
1893.				
Dec. 6.	3·5	27·93	7·98	Sunny.
7.	4·5	35·5	7·88	Sunny.
8.	5·5	36·08	6·56	Sunny.
9.	4·75	26·77	3·53	Overcast.
10.	5	35·5	7·1	Sunny.
11.	4·25	33·75	7·94	Sun, with clouds.
29.	5	37·83	7·56	Sunny.
30.	5	32·01	6·4	Sun, but solution frozen.
31.	7·0	38·99	5·57	Sunny, solution frozen.
1894.				
Jan. 1.	4·5	34·33	7·63	Sunny.
2.	4·5	26·77	5·95	Sunny, some cl'ds.
3.	5	21·53	4·3	Sunny, overcast 2 hours.

* A Paper read before the British Association (Section B), Oxford Meeting, 1894.

* A Paper read before the British Association (Section B), Oxford Meeting, 1894.

Date.	No. of hours.	Total m.grms. Iodine per 100 c.c.	Hour value.	Conditions.
4.	4·5	19·78	4·39	Overcast.
5.	4·5	20·95	4·65	Very little sun.
6.	4·5	16·35	3·74	No sun, snowing.
7.	5·5	20·99	3·89	No sun.
8.	5·25	19·78	3·77	Overcast most of the day.
9.	4·5	35·5	7·88	Sunny.
10.	5	37·53	7·5	Sunny.
11.	5	42·48	8·45	Sunny.
12.	5	39·86	7·97	Sunny.
13.	5	54·12	10·32	Sunny.
14.	5	34·63	6·92	Sunny.
15.	5·75	38·99	6·78	Sunny ½ hr. after sunset.
16.	5·25	41·61	7·92	Sunny.
17.	5	34·92	6·98	Sunny.
18.	5	22·98	4·59	Cloudy.
19.	5	22·11	4·42	Snowing.
20.	5	35·79	7·15	Sun and clouds.
21.	5·25	44·23	8·42	Sunny.
22.	5·25	42·77	6·14	Sunny.
23.	5	18·62	3·32	Snow all day.
24.	5	21·82	4·36	Snowing.
25.	5·25	43·65	8·31	Sunny.
26.	4·75	24·15	5·08	Snowing.
27.	5·5	48·88	8·88	Sun with clouds.
28.	5·5	73·04	13·28	Sunny.
29.	5·75	46·56	8·09	Overcast.
30.	5·75	58·49	10·17	Fair, not much sun.
31.	5·5	22·89	4·16	Half sun, and overcast.
Feb. 1.	5·75	21·86	3·80	Overcast, snow.
2.	5·75	34·38	5·98	Overcast, snow.
3.	6·5	44·91	6·91	Not much sun.
4.	6	87·17	14·52	Sun all day.
5.	6·5	64·41	9·90	Sunny.
6.	7	38·71	5·53	Sun and clouds.
7.	6·5	72·69	11·18	Sunny.
8.	7	39·89	5·69	Sun and clouds.
9.	7	56·73	8·10	Sun and clouds.
10.	8	58·21	7·27	Sun and clouds.
11.	7	50·83	7·36	Sun and clouds.
12.	7	67·03	9·57	Sunny.
13.	6·25	28·95	4·63	Sun 1½ hrs., then snow.
14.	7	46·98	6·71	Sun, then overcast.
15.	8	52·00	6·50	Sun, then overcast.
16.	5·5	38·11	6·92	Sun, then overcast.
17.	6·5	26·59	4·09	Snow, little sun.
18.	7	55·25	7·89	Sunny.
19.	6·5	36·64	5·63	Sun and clouds.
20.	7	55·84	7·97	Sunny.
21.	6·5	54·96	8·45	Sunny.
22.	7·5	65·25	8·70	Sunny but 1½ hr. after sundown.
23.	7	59·16	8·45	Sun and overcast.
24.	6·75	36·83	5·45	Overcast.
25.	6·75	55·10	8·10	Sun and clouds.
26.	7	32·77	4·48	Snow and rain.
27.	6·75	60·90	9·02	Sunny.
28.	7·25	82·87	11·43	Sun 1 hr. after sundown.

It has been remarked in the Engadine that the amount of sunlight during the winter months has been diminishing, but so far as I have been able to ascertain there is no accurate information upon which a statement of this character can be based. The average value per hour obtained from my experiments last year for the month of January, including the bad days, amounted to 8·41 m.grms. of iodine per 100 c.c. per hour, whilst, as already mentioned, the mean from the above experiments, extending over a longer period, is 7·05. This shows that the average amount of light was less during the 1893-94 season than during the previous one; but I do not think that from the records of two seasons that any deductions can legitimately be made.

I hope to make arrangements for a continuance of this work during the ensuing winter, and should be glad to hear of similar work being carried on at some of the other centres in the High Alps.

ON THE

CHEMISTRY OF COAL FORMATION.*

By J. W. THOMAS. F.I.C., F.C.S.

WITH a view to lead up to the consideration of the "proximate chemical constituents of the various kinds of coal," a short sketch of the chemistry of coal formation will open the question respecting further experiments to increase our knowledge of the subject.

It is to be expected that the age of the coal, and the physical conditions, such as the effect of water, heat, and pressure, should throw considerable light upon the chemistry of coal formation. If the tertiary lignites of Bovey Tracey are placed in position above the upper bituminous coals of the South Wales field, a striking gradation and regularity of change is seen between the lignite and the anthracite, as shown in the accompanying table. The lignites are soft, anthracite is very hard; lignites are wet, anthracite dry; lignites show high hygroscopicity, anthracite low. In the table the physical characters run fairly parallel with the chemical. In East Yorkshire the oolitic coals—jet, for instance—is as hard, and dry, and as little hygroscopic, as anthracite; and so is the highly bituminous Wigan cannel. The Scotch coals also furnish exceptions to the rule, and the physical conditions of the coals of Great Britain is of little value in determining their chemical character; and as there are instances of bituminous coals lying below more anthracite varieties, even the depth of the coal below the surface is no safe criterion of its chemical composition.

The decomposition of peat and wood to-day teaches us more respecting the chemistry of coal formation. The late Dr. Angus Smith showed that the woody fibre of recent decaying moss decomposed much quicker than the resinous and gummy portions, the result being a considerable increase of resinous matter in the older peat, and a corresponding loss of combined oxygen.

Observing the decomposition of wood to-day in the case of larch and pine railway sleepers, we see that the portions where the resinoids are in least quantity are first attacked, the knots and other parts saturated with resin and terpenes being preserved after all the woody fibre has disappeared. We know, too, that decomposition is greatly accelerated by myriads of insect and lower life, all of which appear to dislike resinous matters. Thus in forest decomposition, as well as in peat, there is an increase of resinous matter due to the rapid dissociation of the woody fibre. I am giving attention to the decomposition of wood as further experiments are wanted in this direction.

Turning to the tertiary formation of Bovey Tracey, it is found that, just as in the case of peat and wood decomposition, the lignites have an excess of resinous matter in them; and there is, moreover, a considerable quantity of resin in lumps unmixed with the lignite coal. This resin melts at a low temperature, and the strata do not show the effect of much heat. Hatchett named this resin "retinasphaltum," and it was further examined by the writer (*Chem. Soc. Journal*, 1877). The late Dr. Percy ("Metallurgy," vol. Fuel) mentions coals, apparently of

* A Paper read before the British Association (Section B), Oxford Meeting, 1894.

The Lignites of Bovey Tracey, and Coals of the South Wales Field.

Description.	Soft or hard.	Wet or dry.	Hygroscopicity.	Carbon.	Hydrogen.	Oxygen.	Nitrogen.	Sulphur.	Ash.
			Per cent.	Per cent on dry sample.					
Soft lignite	Soft	Wet	15·0	59·9	6·0	25·0	0·6	1·5	7·0
Compact lignite	Medium.	,,	10·0	66·7	5·5	20·0	0·8	2·0	5·0
Upper carboniferous coal (Mynyddyslwyn)	,,	Medium.	6·0	79·5	5·5	4·5	1·5	3·5	5·5
Pennant coals	Hard	,,	4·0	81·5	5·0	4·5	1·5	3·0	4·5
Semi-bituminous coal	,,	,,	2·5	84·2	4·5	4·0	1·3	2·0	4·0
Steam coal	,,	Dry	1·5	87·8	4·2	3·0	1·0	1·0	3·0
Anthracite coal	Very hard	,,	0·5	91·7	3·5	2·5	0·8	0·5	1·0

tertiary origin, from New Zealand, &c., containing particles of resin. Dr. Hofmann, in his investigations upon the coals of Canada (*Trans. Roy. Soc. Canada*, 1889), showed that certain coals, chiefly of tertiary origin, contained grains of mineral resin disseminated through them. And Mr. Watson Smith (*Journ. Soc. Chem. Ind.*, 1892, 1893) found in the Miike coal of Japan as much as 9·5 per cent of bituminous matter. It must be inferred, therefore, that there is an accumulation of resinoid and bituminous matters in lignite coals, and it is a curious fact that the woody varieties, and even the "leafy" coal of Bovey Tracey, composed of branches and leaves in perfect preservation, contained resinous matters in large excess over that which could have been present in the vegetable material in its normal condition. The same is true of those beds of lignite which have all the appearance of compressed wood. And from a careful study of the Bovey Tracey lignites it is not only evident that conifers and other dicotyledonous trees flourished, yielding much resinous and terpene compounds, but that the condition of vegetation was such that liquid gummy and resinous matters were showered from some of the trees during the tertiary coal period. The yellow resin found in quantity in the Bovey Tracey formation shows that the resinoids in the "leafy" and "woody" coals are not the result of the melting and soakage of the accumulated resinoid matters. As it is admitted, unreservedly, that the Bovey coal is made up of conifers and dicotyledons, the above conclusions may not be much questioned; but what of the coals of the carboniferous age? Where would the showers of liquid gummy and resinous matters come from when the vegetation was monocotyledonous? Witham long ago pointed out the mistake which is frequently made to-day, and he showed, sixty years ago, that dicotyledonous trees formed a large portion of carboniferous coal, remarking, "I must contend that there existed coniferous trees, or such as contained a complicated woody structure in great abundance'.' More recent search has revealed, chiefly in the strata intermediate with the coal beds, many dicotyledons other than conifers; hence there is no evidence wanting to show that true wood formed a large share of the coal of carboniferous age. Mr. Hutton (*Lond. and Edin. Phil. Mag.*, 1833) mentioned that he observed under the microscope that some of the coals of the North of England coal-field contained minute grains of a yellow bituminous resinoid, so volatile as to be easily expelled by heat without altering the structure of the coal; and, since then, similar observations have been made.

These facts show that what was true of the Bovey Tracey lignite formation, is true also of coals of the carboniferous age, and there seems every probability that not only did conifers and other dicotyledonous trees flourish during the carboniferous period, but that much liquid gummy and resinous matters were showered from the trees upon the dried and decomposing material on the surface. It is well known that various trees, like the lime, for instance, during the flowering period, often shed enough saccharine matter to render its leaves and the grass underneath covered with the saccharine material; and not unfrequently coniferous trees, like the Scotch fir, shower terpenes and resinoid matters upon the ground beneath. It is to this behaviour of tree life I attach much importance, as having a weighty bearing upon the chemistry of coal formation, not only during the tertiary, but also during the carboniferous age.

It has long been an enigma to botanists and geologists why the forms of the delicate ferns of the carboniferous coal period should be so perfectly preserved, whilst so little of the structure of the woody material is discernible. My opinion is that these ferns and delicate undergrowth, when dying and drying, became saturated with liquid resinous matters falling from the trees, and, in this way, were preserved from putrefaction, to imprint their beautiful forms upon the shale and rock above the coal, and in other positions.

From a careful consideration of the condition of vegetation during the carboniferous age, and the decomposition which ensued, I think that the chemical nature of coal, as we find it, is the result, not so much of heat and pressure and decomposition in its deeply buried condition, as upon the character of the primary decomposition which took place at or near the surface, together with the nature of the material from which the coal was formed.

Starting with the bituminous shales, like those used by the Young Candle Company, and at the Pumpherston Works in Scotland, I believe that there, as shown in the mineral strata, huge forests flourished from which the woody fibre was eliminated by surface decomposition, only resinoid matters remaining. The high percentage of mineral matter favours this view.

Resinous vegetation, without much dicotyledons, or if with dicotyledonous trees, much surface decomposition, by long-continued exposure would produce Scotch cannel, rich bituminous coals, Wigan cannel, &c.

A luxurious resinous and dicotyledonous vegetation, without much surface decomposition, probably gave rise to semi-bituminous, steam, and anthracite coal, assisted, of course, by heat and pressure.

Now as to our present knowledge of coal itself.

1. It contains water, and retains some after long exposure in dry air. As shown in the table, the quantity of water retained by a coal after drying at ordinary temperatures is, as a rule, proportionate to the age of the coal —being highest in lignite and lowest in anthracite. Jet, and numerous coals of the carboniferous age in various coal-fields are exceptions to the rule. Some lignites contain 30 per cent of water in the natural condition, but the better qualities do not hold more than 20 per cent, and this is reduced by air drying to 10 per cent. Such coals as are used for fuel in this country rarely hold more than 5 per cent after being air dried. Coals which we ship abroad, in their air-dried condition, generally contain less than 3 per cent of moisture; whilst steam and anthracite coal from dry seams do not hold more than 1 per cent of moisture. Coals won from seams to which water gains access contain much larger quantities of water; but I am referring now to the hygroscopicity of coal.

The point I wish to emphasize is, not the quantity of moisture air-dried coal contains, but to call attention to how this moisture is held. If the water still retained in an air-dried sample of coal be driven off by heat, and the dried coal afterwards exposed in a moist atmosphere, the moisture is re-absorbed at a very quick rate; and so great is the hygroscopicity of some coals that it is not possible to estimate the water in an open vessel, as the weighing

cannot be done quickly enough to prevent re-absorption. Dr. Hoffmann, of the Canadian Geological Survey, has shown that a portion of the water in coal is most obstinately held, and there is no doubt, I think, that it exists in chemical combination. In the deep dry steam and anthracite coals, as they occur in their seams, there is, probably, no moisture, but these are very hygroscopic to a certain point, and in the analyses of coal the hygroscopicity has not received due attention. Furthermore, it seems to me that the hygroscopicity of coal is the key to the property of spontaneous combustion, and should be made the subject of further experiment.

2. Coal contains the gases, oily matters, and solids of the paraffin series. In my experiments on the gases enclosed in various coals I obtained gases and liquids of the paraffin series, and, in one instance, white solid paraffin from a coal of carboniferous age. Mr. Watson Smith's experiments (*Journ. Soc. Chem. Ind.*, 1893) show conclusively that liquid and solid paraffins exist ready formed in coal, but they rarely exceed 1 per cent in coals of the carboniferous period.

3. Coals contain 0·5 to 10 per cent of ash or mineral matter in good samples, and from 0·5 to 4 per cent of sulphur generally present as disulphide FeS_2 in coals of carboniferous age. In lignites it frequently occurs in organic combination.

4. The bulk of coal consists of carbon, hydrogen, and oxygen, with from 0·5 to 2 per cent of nitrogen. How the nitrogen is combined is not known. The same remark applies to the carbon, some of which doubtless is in combination with hydrogen. How much of the carbon is free and how much is in combination with hydrogen will, most probably, never be known. The oxygen is generally regarded as being combined with hydrogen, but I do not think that this is the case with the dry deep coals containing occluded marsh-gas; some oxycarbon compound containing hydrogen is probably the condition.

In conclusion, I suggest that further experiments be made in the following directions:—

1. Upon the decomposition of dicotyledons with a view to throw light upon the formation of coal.

2. Upon the hygroscopicity of coal; and to study its bearing upon the spontaneous combustion of coal on board ship.

3. Upon the coals from all the British coal-fields to determine the quantity, and, if possible, the constituents soluble in gasolene (petroleum ether), or benzine, as employed by Mr. Watson Smith.

4. To act upon the various coals with a weak solution of potassic hydrate.

SEPARATION AND DETERMINATION OF TIN AND ANTIMONY IN AN ALLOY.

By M. MANGIN.

The separation of antimony and tin presents considerable difficulties, especially when the two substances are alloyed with other metals precipitable by sulphuretted hydrogen, such, *e.g.*, as anti-friction metal, for in this case it is scarcely practicable to transform the two metals into sulphides, their complete solution in alkaline sulphides for their separation from other metals being long and troublesome.

When we have to do with an alloy of this sort it is best to attack it with nitric acid, which dissolves the other metals and converts the tin and the antimony into insoluble oxides. We collect these oxides, wash, ignite, and weigh. Here arises the difficulty, for if we have succeeded in separating the antimony and the tin from the other metals, it is not easy to determine them in this state. A number of methods have been proposed, all of which leave something to be desired, because they present causes of error or because they are tedious and difficult in execution. Some chemists have sought to reduce the oxides in the dry way, whilst others have attempted to dissolve them and to re-precipitate the metals.

I omit the electrolytic method, which is useful only if we possess the apparatus, and if we have already succeeded in obtaining the two metals tin and antimony alone in a liquid.

I thought it useless to seek for circuitous methods for dissolving the two ignited oxides, and that they might be easily reduced by causing nascent hydrogen to act upon them. Experiment and the data of thermo-chemistry confirm this expectation. In fact, if we cause hydrochloric acid to act upon antimony oxide, the following reaction takes place in presence of tin:—

$$Sb_2O_4 + 8HCl \text{ diss.} + 4Sn = 2Sb + 4H_2O + 4SnCl_2 \text{ diss.} +$$
$$+ (4{\cdot}69,\ 0 + 481,\ 2 - 248{\cdot}6 - 8{\cdot}39,\ 3) = +37{\cdot}8).$$

The same calculation may easily be established for tin.

The following is the method of operation which I have found satisfactory:—

After having ignited the two oxides and taken their weight, they are placed in a beaker of Bohemian glass along with a plate or a ball of pure tin, some water, and hydrochloric acid. The beaker is set on the sand-bath (for 1·5 to 2 grms. of oxides three hours are required in a very acid liquid). The antimony begins to be reduced, and the tin oxide is converted into chloride. It is well to stir from time to time to renew the contact. We know that the reaction is at an end when we no longer perceive a trace of oxides. At this moment the liquid is perfectly clear, and the reduced metal, very black, is precipitated rapidly to the bottom of the vessel on withdrawing the source of heat.

The liquid is decanted and the precipitate is washed in the glass with water which has been boiled and allowed to cool with exclusion of air.

The precipitate is collected on a filter, washed with water and then with alcohol, dried in the stove, and weighed. We thus obtain the exact weight of the antimony. There is no appreciable oxidation of the antimony.

Knowing the weight of the ignited oxides and that of the antimony, we find the weight of the tin by a very simple calculation.

Let A be the weight of the antimony; we multiply this number by 1·262 to find the corresponding weight of antimony oxide, which is deducted from the weight M of the mixture of the two oxides.

M − A 1·262 = the weight of tin oxide; this latter multiplied by 0·78667 gives the weight of tin contained in the alloy.—*Comptes Rendus*, cxix., p. 224.

NEW RESEARCHES ON CHROMIUM.

By HENRY MOISSAN.

Chromium, the discovery of which is due to Vauquelin, has already met with numerous applications. It has been little utilised in the metallic state on account of the difficulty of its preparation. Hitherto it has never been obtained in notable quantities, and when it has been desired to utilise its wonderful properties for the manufacture of chrome steels, it has been necessary to prepare ferrochrome, an alloy of iron and chrome very rich in carbon.

The presence of iron and of carbon in this compound has prevented this study from being extended, and we do not know the alloys which chromium can form with the other metals.

The researches which we now publish will probably permit us to fill up this deficiency.

Preparation.—We have already indicated how easy it is, by means of the high temperature produced in our electric furnace, to reduce chromium sesquioxide by means of coke either in an intermittent or a continuous

apparatus. In the latter case we used an electric furnace containing a sloping coke-tube, receiving at its upper end the agglomerated mixture of sesquioxide and of carbon, and allowing the liquid metal to flow out at the lower end. This coke-tube was heated in our model reverberatory electric furnace with movable electrodes.

By means of this apparatus it was easy for us to prepare the 20 kilos. of metallic chrome which we have the honour of submitting to the Academy.

The cast-metal thus obtained contains large quantities of carbon. We have studied the different conditions of the formation of this metal, and we have been able to prepare two definite crystalline compounds of chrome and carbon.

Carbide of the Formula C_2Cr_3.—If in the crucible of the electric furnace we heat for ten to fifteen minutes metallic chrome in presence of a large excess of charcoal (employing 350 ampères and 70 volts), we obtain a brittle ingot full of crystals of chromium carbide answering to the formula C_2Cr_3. This carbide appears in very brilliant laminæ of a fatty lustre, not attackable by concentrated hydrochloric acid, by nitric acid, fuming and hydrated, or by aqua regia, but slowly acted on by dilute hydrochloric acid. Melting potassa has little action upon it, but melted potassium nitrate destroys it with ease. Its specific gravity is 5·62. It does not decompose water either at the common temperature or at 100°.

Carbide of the Formula CCr_4.—In the numerous preparations of cast chrome which we have made, we have sometimes seen the surface of the ingots covered with needles of a bronzy appearance, and often from 1 to 2 c.m. in length. These crystals answer to the formula CCr_4. They are also found in the shape of brilliant needles in the hollow nodules formed in the midst of the cast chrome. Their specific gravity is 6·75.

Crystalline Chromium.—We have attempted to refine this cast chrome by heating it in presence of an excess of oxide. It is thus practicable to remove the carbon, but the metal thus obtained is saturated with oxygen; it is, from a metallurgical point of view, a burnt metal.

It was then refined in presence of melted lime, and we have been able, by operating each time on a quantity of from ½ to 1 kilo. of metal, to remove the larger part of the carbon contained in the chrome. We know, in fact, how easily carbon and lime combine to form calcium acetylide.

We have utilised this reaction, and it has commonly yielded a metal of a fine grain containing from 1·5 to 1·9 of carbon. When chrome is thus purified it crystallises with great facility. We have often obtained very fine specimens of crystallised chrome, in which the crystals attained the length of from 3 to 4 m.m. These crystals have at first sight the appearance of cubes and octahedra. Their grouping recalls that of crystalline masses of bismuth.

Frémy had previously shown the possibility of obtaining crystalline chromium by the action of sodium upon chromium chloride.

Chromium Free from Carbon.—The method of refining by melting lime does not yield chromium absolutely decarbonised. When the chrome is sufficiently pure there is produced an inverse reaction in presence of the liquid lime and of the furnace gases. All the metal is brought back to the state of finely crystallised double chromium and calcium oxide.

We have then taken this double oxide which is so easily produced in our electric furnaces; we have lined with it a furnace of quicklime, and in the midst of which we have re-melted the cast chrome. Under these novel conditions the refining is produced, and we obtain a brilliant metal which can easily be filed and polished. This is pure chromium, which on analysis no longer shows a trace of carbon.

Physical Properties. — The specific gravity of pure chrome at 20° is 6·92 (the mean of three experiments).

With the oxygen blowpipe at the point of the blue flame, refined cast chrome yields brilliant sparks, burns partially, but appears to melt superficially only by reason of the excess of heat developed by this combustion. The fusion is never complete: it is only superficial, and the melted portion is still rich in carbon. In the closed lime furnace which Deville and Debray used for melting platinum, we were not able to melt cast chrome (at 2 per cent of carbon) with the oxyhydrogen blowpipe after forty-five minutes of action. The fragment of the cast metal which was struck by the extremity of the blue flame was alone melted in part in consequence of the phenomenon of oxidation just mentioned.

When the chrome is very free from carbon it burns rapidly, and its combustion before the blowpipe is still more brilliant than that of iron. The oxidation is rapidly completed, and after the experiment there remains a rounded fragment of melted chromic oxide.

Pure chromium is more infusible than cast chromium; its melting-point is notably higher than that of platinum, and it cannot be attained by means of the oxygen blowpipe. On the contrary, in the electric furnace melted chromium has the aspect of a brilliant liquid, very fluid, displaying in the crucible the appearance and the mobility of mercury. It can even be taken out of the electric furnace and poured into an ingot-mold. By utilising as an electric arc the heat yielded by a current of 1000 ampères and 70 volts, we were able in a furnace of sufficient size to produce at once 10 kilos. of refined cast chrome and to run it with ease.

The following is a complete analysis of the cast chrome:—

Chromium	97·14
Carbon	1·69
Iron	0·60
Silicon	0·39
Calcium	traces

Pure chromium free from iron presented no action on the magnetic needle.

Chromium carbide of the composition C_2Cr_3 scratches quartz with ease and even topaz, but it has no action on corundum. CCr_4 scratches glass deeply and quartz less easily. Pure chromium has no action upon quartz, and scratches glass with great difficulty. Some fragments of pure chromium do not scratch glass at all.

Fine-grained cast chrome with properties of carbon ranging between 1·5 and 3 can only be wrought and polished on wheels fed with diamond dust.

On the contrary, refined chromium free from carbon may be easily filed, taking the polish of iron and presenting a fine lustre a little whiter than that of iron.

Chemical Properties.—Cast chrome is not attacked by the air on exposure to carbonic acid and moisture.

Pure chromium well polished is slightly tarnished after some days' exposure to moist air, but this slight oxidation is superficial and does not extend.

Chromium may be regarded as unalterable in the air. If heated in oxygen to 2000° it burns, giving off numerous sparks more brilliant than those produced by iron.

Chrome filings heated to 700° in the vapour of sulphur become incandescent and are converted into chromium sulphide.

Pure chromium placed in a crucible lined with charcoal and heated in the violent fire of a forge yields carbide CCr_4 in the form of needles. At the temperature of the electric furnace there is formed the crystalline C_2Cr_3.

Silicon combines readily with chromium. On heating in the electric furnace a mixture of chromium and silicon, we obtain a silicide very well crystallised, very hard, scratching ruby easily, not attacked by acids, by aqua regia, by potassa, and by potassium nitrate in fusion.

Boron combines with chromium in the electric furnace under the same conditions, and yields a crystalline boride scarcely attackable by acids and having a great hardness.

Gaseous hydrochloric acid reacts upon chromium at dull redness, forming a crystalline monochloride.

A solution of hydrochloric acid attacks chromium very slowly in cold and more rapidly in heat. The dilute acid produces nothing at common temperatures, but at ebullition the action is much more lively. Under the action of an electric current chromium placed at the positive pole is dissolved in the dilute acid.

Concentrated sulphuric acid at the ebullition-point disengages sulphurous acid, and the liquid takes a dark colour. The dilute acid acts slowly in heat, and if the reaction takes place in the absence of air, the blue chromous sulphate is formed.

Fuming nitric acid and aqua regia have no action upon chromium whether in cold or heat. With dilute nitric acid the action is very slow.

Solution of mercuric chloride acts very slowly on powdered chromium, forming chromic chloride.

At 1200° chromium, if kept in a current of hydrogen sulphide, is entirely converted into a melted sulphide of a crystalline appearance.

At the same temperature carbonic acid attacks chromium superficially, and the metal is covered with a green layer of oxide mixed with carbon.

Carbon monoxide is reduced at 1200° by the metal, with formation of a superficial deposit of sesquioxide and conversion of the metal into carbide. This reaction explains the difficulty of refining.

Fused potassium nitrate acts energetically upon chromium at dull redness. The experiment is improved if melting potassium chlorate is used instead of nitrate. The chromium floats with a splendid incandescence upon the surface of the liquid.

Melting potassa does not appreciably attack chromium at dull redness.

This method of preparing chromium renders the formation of the alloys of this metal practicable. If combined either with aluminium or copper, it gives interesting results.

Pure copper, alloyed with 0·5 per cent of chromium, has its resistance nearly doubled, and the alloy is less affected by moist air than is copper.—*Comptes Rendus*, cxix., p. 185.

A NEW SULPHURETTED HYDROGEN APPARATUS.

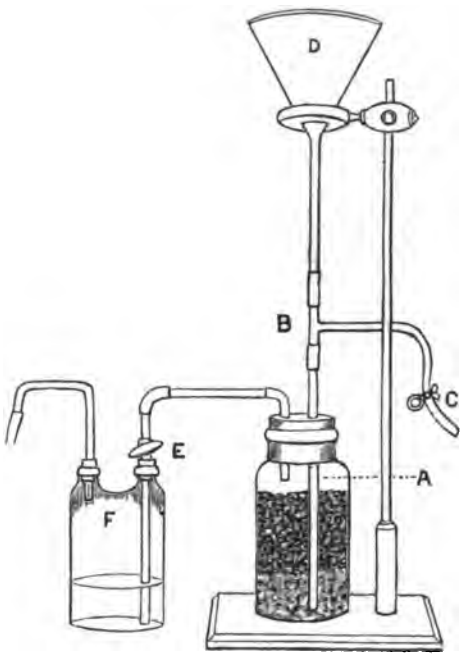
By J. F. LIVERSEEGE, F.I.C.

Most of the arrangements used for preparing sulphuretted hydrogen on a small scale suffer from either or both of the following disadvantages:—(1) The size of the hole through which the ferrous sulphide is introduced to the generator requires the sulphide to be crushed rather fine, with the result that there is a good deal of powder which gets into the acid bottle and continually generates the gas. (2) The tube between the acid bottle and the generator is small and is frequently stopped up.

To avoid these troubles, some four years ago I devised the following arrangement:—

The generator, A, is a pint green glass wide-mouth bottle, with broken glass at the bottom an inch deep, and on it the lumps of sulphide; as the neck is 1¼ inches in diameter, fair sized pieces can be put in. This is closed gas-tight with a cork or rubber bung coated with paraffin wax; through it pass two glass tubes; one, just through the cork, is connected with a pint Woulff's bottle, F, for washing the gas; the other, $\frac{1}{10}$th inch inside diameter, reaches nearly to the bottom of the generator, and is connected by means of a T-piece, B, with a large glass funnel, D. The other leg is closed by a rubber tube and pinchcock, C.

A little water is put in the funnel and commercial hydrochloric acid added. As the gas is generated, the liquid is forced up into the funnel, the layer of glass at the bottom preventing the sulphide soaking in the acid. A glass stopcock, E, is used for regulating the supply of the



gas. When no more gas is required, the pinchcock, C, is removed, and the acid runs out through the side tube into a bottle for future use with more acid if necessary.

CORRESPONDENCE.

SHOULD CHEMICAL TECHNOLOGY HAVE A PLACE IN OUR UNIVERSITIES AND UNIVERSITY COLLEGES?

To the Editor of the Chemical News.

Sir,—Mr. E. C. C. Stanford, in his Presidential Address before the Society of Chemical Industry, in Edinburgh last month, asked the question—"Is not our journal now rather ahead of the national scientific and technical teaching?"

I apprehend he meant by this that it had become a question, amongst others, how many young men leaving our colleges were able to so digest and assimilate the contents of the *Journal* of the Society, as to yield results of value in the factory of any chemical manufacturer employing them?

In any case it may be pointed out that this *Journal* has many readers on the Continent; and granting that *there*, university and college instruction with reference to chemical technology, is of a sounder, more thorough, and far-reaching character than here, as indeed it unmistakeably is, and also that young foreigners coming to England to seek their fortunes or complete their education, may, if they like, join this Society and study its journal, Mr. Stanford's question may receive further and legitimate expansion, and on this wise: "Will not the *Journal of the Society of Chemical Industry*, if ahead of the national scientific and technical training, but well abreast of that of Germany and France, whilst an unwieldy im-

plement under the former conditions, prove a thoroughly useful one under the latter?" The boast then that "*We, in England, run the best journal of applied chemistry in the world*," would be a boast in such case that would be continually subject to the humiliating mitigation involved in a query that would seem to come like a mocking echo across the channel—"*For whom?*"—unless we and our Government quickly see to it that our universities and colleges are properly and universally equipped and fortified, as regards both chemistry and the specialised branch of knowledge in question.

Dr. Ludwig Mond, F.R.S., who knows the Continental calibre accurately, and loves England, the country of his choice, and desires her highest welfare in this direction, utters a warning note in the very nobility of the example he has set in founding the Davy-Faraday Research Laboratory of the Royal Institution; for chemical technology in the highest sense involves and includes *a continual course of specialised chemical research.*

I have just been reading, in the *Chemiker Zeitung* of August 8 a remarkable testimony of one of the greatest of Continental chemists, Professor Victor Meyer, of Heidelberg (formerly of Göttingen and Zürich), as to the training and instruction in chemical technology in German universities, and I give below a precise translation of this article of Victor Meyer's, and will let it speak for itself. No comment would be necessary from me, though I might perhaps re-echo that saying of Mr. Stanford's in the Address referred to, of which Prof. T. E. Thorpe subsequently predicted that it would one day become classical, to wit—"*We ought for shame to hide our national head in our national pocket, which is quite big enough, if we will not put our hands there, to supply such national needs.*"—I am, &c.,

WATSON SMITH.

34, Upper Park Road,
Haverstock Hill, N.W.

REMARKS ON THE STUDY OF CHEMICAL TECHNOLOGY IN UNIVERSITIES.

By Professor VICTOR MEYER (Heidelberg University).

At a meeting held in Cologne on the 21st of May, Dr. E. O. v. Lippmann expressed views on this subject which I in great measure wholly endorse. Amongst other things, he stated that—"For the 2000 to 3000 chemical students annually passing through German universities, scarcely any opportunity for acquiring a knowledge of technology was presented."

The high repute in which the speaker is held, as technologist, investigator, and historian, gives a special significance to the opinions expressed by him, and impels me to offer some slight correction to the statement, and to give a brief statement of certain matters of fact known to me.

Whilst on the one hand it may be conceded that in many universities, opportunity of technological training is in no wise as it should be, yet, on the other hand, it must be admitted that in some universities which are chiefly sought by students of chemistry, regular and very thorough courses of lectures are given on general chemical technology.

For example, in Göttingen, where I formerly worked, lectures in chemical technology are given by Prof. Tollens and Dr. Lorenz. Since Whitsuntide, Dr. Ferdinand Fischer has in addition given further lectures in chemical technology illustrated by numerous visits to works, exercises in calculation, and drawings of apparatus and plant. In Heidelberg, regular courses of lectures are given, comprising all the more important branches of chemical technology, and I will now briefly make more detailed reference to these. Besides a three hours' course on chemical technology, which Prof. A. Schmidt has given for years, principally for the requirements of commercial men, &c., at our university, there are given regularly courses of lectures of a thorough-going character, on general chemical technology, dye-stuffs, dyeing, and metallurgy, by Professors P. Jacobson, L. Gattermann, and A. Schmidt. Professor Jacobson lectures on the whole subject of chemical technology with the exception of metallurgy, dyes, and dyeing, for two hours per week for two Semesters. *In the first Semester*, the subject of the treatment of inorganic raw materials is chosen, *e.g.*, sulphuric acid, nitric acid, common salt, soda, hydrochloric acid, and chlorine; bleaching-powder, potash salts, lime and cements; glass and earthenware; and artificial manures.

In the second Semester, the processes which are concerned in the treatment of organic raw materials are dealt with:—Valuation of fuels and combustibles, and processes of destructive distillation; the fermentation industries, sugar, starch, cellulose; stearin and soap industries. In connection with this course there are numerous excursions to chemical works—a matter rendered feasible through the extreme kindness and generosity of the many chemical factories in our neighbourhood. The students of this two Semester course have actually visited in this way the following factories:—

The Chemische Fabrik Wohlgelegen des Vereins Chemischer Fabriken.—Sulphuric acid, Leblanc soda, caustic, bleach, hyposulphite, nitric acid, carbonate of magnesia, alumina, alum, &c.
Chemische Fabrik Heilbronn.—Ammonia-soda.
Salzwerk Heilbronn.
Chem. Fabrik Rhenania, Rheinau.—Sulphuric acid, sulphate of soda, and hydrochloric acid (Hargreave's process), Deacon's and Weldon's processes, bleach, &c.
Portland Cement Works in Heidelberg.
Badische Earthenware and Stoneware Factory in Friedrichsfeld.
The Frankfort Gas Works.
Fabrik Chemisch-tech. Producte of Simon and Dürkheim, Offenbach a/M.—Soaps.
Chem. Fabrik Lindenhof, von Weyl and Co.—Tar distilling.
Pfälzische Presshefen und Sprit Fabrik, in Ludwigshafen.—Yeast manufacture and spirit distilling.
The Edinger Brewery. Sugar Refinery at Frankenthal. *Vereinigte Holzindustrie Frankenthal. Maschinen und Armatur Fabrik vorm. Klein, Schanzlin, and Becker*, Frankenthal.

In further special lectures, Prof. A. Schmidt deals with metallurgy, and Prof. L. Gattermann with the coal-tar colours, with practical dye tests and trials.

Now the instruction in chemical technology above described is distinguished from that given in technical high schools (technischen Hochschulen), as must be evident, in several essential particulars. Chiefly, it is of considerably greater comprehensiveness in the technical high schools, and special laboratories are provided in which special theses of technological character are worked out. The training in constructive design and technical drawing is on definitely arranged lines.

In the examinations, and for the diplomas, a greater degree of thoroughness in chemical technology is demanded, and the instructors are frequently men who have themselves served for a long time in the factory, and have acquired considerable reputation as technologists.

In spite of these considerable differences, the report just given shows that the demand of Dr. Lippmann, "that the students of the universities should have facilities granted them for enjoying the advantages of instruction in technology," in some universities has already found practical acquiescence, and that, indeed, the present condition of the technical instruction at our universities is not everywhere so unsatisfactory as he made it appear in the picture drawn by him.

The opportunity for acquiring a general knowledge of chemical industry is, in point of fact, offered in certain universities, and—at least I can vouch for this in Heidel-

berg—it is utilised by our students in the very numerous applications for admission to the lectures and excursions.

But I coincide completely with Dr. Lippmann in his wish, not only for an extension of this technical instruction in our universities in its present scope, but also for the further development of the same, and I would add thereto the expression of my own opinion that instruction in technical drawing, and building- and machine-construction, ought not to be omitted in the curriculum of any university in which numerous young chemists seek their education, and are likely ultimately to desire occupation in factories and works.

THE PERIODIC LAW.

To the Editor of the Chemical News.

SIR,—In the printed report of Lord Salisbury's Presidential Address to the British Association, the following passage occurs :—"In the last few years the same enigma has been approached from another point of view by Professor Mendeleeff. The periodic law which he has discovered reflects on him all the honour that can be earned by ingenious, laborious, and successful research." Before the Address was delivered, Lord Salisbury became aware of the claim of Newlands as the first discoverer of the periodic law, and the words actually spoken in the Sheldonian Theatre were :—"In the last few years the same enigma has been approached from another point of view by our own countryman Newlands and by Professor Mendeleeff. The periodic law which they have discovered, &c."

Unfortunately, the Address was already printed and distributed to the press before the alteration was made. The claim of Mr. Newlands is secured to him by the award of the Davy Medal in 1887 by the Council of the Royal Society; but I will thank you to insert this letter, lest it should be thought that the President of the British Association had ignored it.—I am, &c.,

ONE OF THE AUDIENCE.

A CORRECTION.

To the Editor of the Chemical News.

SIR,—In our paper on "Some Analytical Constants of Seal Oil," published in the CHEMICAL NEWS (vol. lxx., p. 1), the numbers given in the column under "Reichert's test," represent the amounts of caustic potash (in grms.) required to neutralise the volatile fatty acids obtained from 100 grms. of the oil and not from 2·5 grms. We had not observed that the insufficient explanation given by us of these numbers amounts to an actual mis-statement. We mentioned the 2·5 grms. merely to show that this quantity, and not 5 grms., was taken by us for the experiment.—We are, &c.,

ALFRED C. CHAPMAN,
J. F. ROLFE.

Sophistication of Foods.—It may be remembered that when the Somerset House chemists were appointed as a Court of Appeal from the decisions of the Public Analysts we pointed out certain objections to the project. At the recent meeting of the British Institute of Public Health, Dr. Hehner—certainly no mean authority—protested emphatically against the conduct of the official chemists. He complains that the adulterations of butter and milk are decidedly increasing, that samples of milk are allowed to stand for weeks unexamined, and that when at last analysed the results are accepted as the basis of legal decisions. The amount of water permissible in butter has not been fixed, a fact which seriously injures the Irish butter trade. Attention does not seem to have been officially drawn to the manufacture (or sale) of spurious coffee-beans.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxix., No. 4, July 23, 1894.

On a New Series of Sulpho-phosphides, the Thiohypophosphates.—C. Friedel.—The author proceeds as follows :—A tube of hard Bohemian glass containing the metal and the phosphorus sulphide, or sulphur and red phosphorus in suitable proportions, is sealed before the lamp so as not to exceed 20 or 25 c.m. in length. It is placed in an iron tube, in which it is bedded on and covered with sand. In this manner he has obtained iron thiohypophosphate, $P_2S_6Fe_2$, crystallised in brilliant hexagonal plates of a blackish grey, but brown by transmitted light. They dissolve in nitric acid and still better in the same acid with the addition of potassium chlorate. The corresponding aluminium compound forms long transparent crystalline laminæ which are decomposed by water, with the liberation of sulphuretted hydrogen. The zinc compound forms crystalline masses of a very pale yellow. Copper thiohypophosphate, $P_2S_6Cu_2$, is of a yellowish brown, brittle and transparent. The lead compound, $P_2S_6Pb_2$, is a crystalline hygroscopic mass of an orange colour. The mercurial salt, $P_2S_6Hg_2$, is crystalline and of a yellow colour. It is slowly attacked by boiling water, with an escape of sulphuretted hydrogen. With due care a quantity of the substance may be sublimed *in vacuo*. Two tin compounds have been obtained, $P_2S_6Sn_2$ and P_2S_6Sn.

The Electrolysis of Copper Sulphate.—A. Chassy.—On the electrolysis of copper in heat there is often obtained a violet-red deposit. It consists of red cuprous oxide and may be considered as artificial cuprite. An interesting fact is the difference between the weight of this deposit and the weight of that obtained at the negative electrode of a cold sulphate of copper voltmeter in series with the hot voltmeter. The weight of the latter is always considerably in excess. It is therefore necessary to beware of inferring the intensity of a current from measurements effected with a hot solution of copper sulphate.

On Manganese Steel.—H. Le Chatelier.—Manganese steel (13 per cent of manganese) is not magnetic, and of all the alloys of iron it is the one which presents the highest electric resistance. It is the more malleable the more energetically it has been tempered. There is a second allotropic variety which is magnetic. M. Le Chatelier has determined the conditions of the transformation of the two varieties of manganese steel into each other. To convert the non-magnetic into the magnetic metal it is heated to 550° from one to two hours. To convert the magnetic metal into the non-magnetic metal it is heated to 800° and cooled rapidly, so that the inverse change may not be produced between 500° and 600°. The expansion of the two varieties of manganese steel has been found alike which excludes the existence of a change of dimension at the point of transformation. Manganese steel tempered in water on re-heating undergoes a contraction of 0·4 m.m. in 100 m.m.

On Metaphthalodicyanacetic Ether.—M. Locher.—The two phthalodicyanacetic ethers are the isomers of the orthophthalodicyanacetic ether which Muller obtained by causing ordinary phthalyl to react in the cold upon sodiocyanacetic ether.

Organo-metallic Compounds of Borneol, Camphor, and Monochlorocamphor with Aluminium Chloride.—G. Perrier.—The borneol compound, $(C_{10}H_{18}O)_2Al_2Cl_6$, is very instable; benzene, toluene, and chloroform decompose it partially in heat, with liberation of hydrochloric acid. Water decomposes it briskly, giving a solution of

aluminium chloride and reproducing borneol. The camphor compound, $(C_{10}H_{16}O)_2Al_2Cl_6$, is decomposed by water, with the reproduction of camphor. The monochloro-compound, $(C_{10}H_{15}ClO)_2Al_2Cl_6$, is very instable in air and is decomposed by water.

On a New Acid, the Isocampholic Acid.—M. Guerbet.—This acid corresponds to the formula $C_{10}H_{18}O_2$. It is non-basic; it is a colourless liquid, of an oily consistence and an unpleasant odour. It is almost insoluble in water, but miscible with alcohol and ether. It does not fix bromine. It boils under the ordinary pressure at 256°—257°, with partial decomposition. Its specific gravity at 0° is 0·9941. Its rotatory power is $\alpha_D = +24° 38'$. The properties of isocampholic acid and its derivatives show that it cannot be confounded with any acid of the same composition hitherto known.

Action of Phosphorus Pentachloride upon Tetrachloroquinone.—E. Barral.—The body obtained by the action of phosphorus pentachloride upon chloranil is hexachloro-benzene paradichloride. Chloranil is a chlorodiketon and quinone a diketon.

Oil of Pelargonium from Reunion.—Ph. Barbier and L. Bouveault.—Oil of pelargonium contains at least six distinct substances, among which the rhodinol of pelargonium predominates.

Condensation of Formic Aldehyd with Alcohols of the Fatty Series in presence of Hydrochloric Acid.—C. Favre.—The authors have obtained an entire series of monochloric ethers derived from formic aldehyd and the alcohols of the fatty series, according to the reaction $HCOH + ROH + HCl = CH_2Cl.OR + H_2O$.

Existence of Hydrogen Peroxide in Green Plants.—A. Bach.—None of the usual reagents for hydrogen peroxide can give certain or unquestionable results as to the existence of this substance in plants. We have as little reason to assert it as to deny it.

Presence of Several Distinct Chlorophylls in one and the same Vegetable Species.—A. Etard.—From the total chlorophyllic substance, whether extracted by means of alcohol or of carbon disulphide, the author has separated and analysed four distinct chlorophylls perfectly definite. They will be described separately.

MISCELLANEOUS.

The German Solvay Co. of Bernburg has prepared plans for the establishment of work at Osternienburg, for the electrolytical production of caustic potash, chlorine, and chlorite.

A State Chemical Laboratory for Uruguay.—We learn that the Minister of Finance of the Republic of Uruguay has recently proposed the establishment of a State Chemical Laboratory.

An Indian Chemical Department.—It is stated that the Government of India has under consideration a scheme for the constitution of a separate Chemical Department for the whole of India, for the purpose of training medical practitioners as chemical analysers.

Sewage of Aldershot Camp. — The sewage of the Aldershot Camp is disposed of upon a sewage farm. According to an official inspection this farm is a pestilent sewage marsh, with stagnant pools of evil-smelling liquid. According to the Surrey Medical Officer, the health not only of the troops, but of the inhabitants of the neighbourhood, is in danger, and the attention of the War Department has been drawn to the mischief.

Proportion of Solids in Milk. — According to A. Schmid, chemist to the Swiss Canton Thurgau (*Chem. Zeit.*), in 76 per cent of the samples of milk examined the total solids exceeded 12·5 per cent; in 20 it ranged from 12·5 to 12; and in 4 only did it fall below 12 per cent. Hence it appears that the demand of 12 per cent solids (and 3 per cent fat) as a minimum is not exorbitant. According to the same journal, 12 per cent solids, including 3 per cent fat, is the minimum permissible in Basle city.

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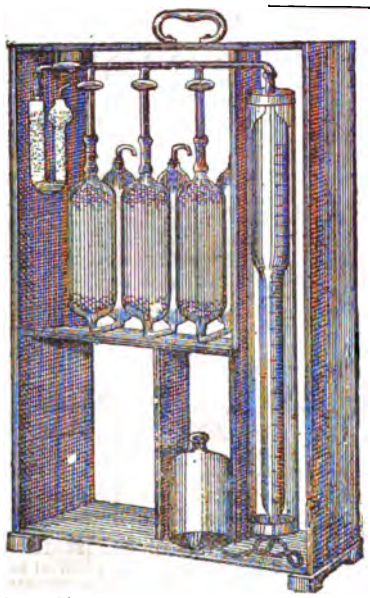

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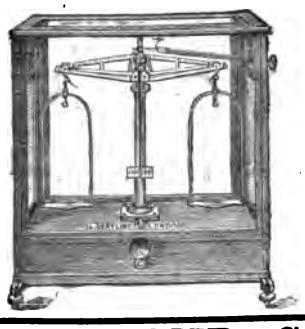

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THE CHEMICAL NEWS.

Vol. LXX., No. 1814.

AN OLD BUT FLOURISHING BLUNDER IN MEDICAL CHEMISTRY.

By CHAS. W. FOLKARD.

"Lithic urate is more soluble than any other of these salts [the urates]. Hence lithia water is occasionally prescribed to gouty patients and to others who suffer from a superabundance of uric acid." . . .

The above is an extract from p. 773, Part III., of Miller's "Elements of Chemistry," 4th edition, published in 1869, and there is sufficient semblance of truth in it to mislead those who are able to devote but a few months to the study of chemistry, as is the case with the majority of medical students.

Although the paragraph quoted was omitted in the new edition published in 1880 it would seem that no attention was called to the subject, for sufferers from a too abundant secretion of uric acid have been treated up to the present time on an erroneous assumption, proceeding from the "little knowledge" which is admittedly so dangerous, and which is also doubtless responsible for the practice of exhibiting chlorate of potash in cases of blood poisoning, "to oxidise and destroy the poison in the blood," whereas every chemist is aware that in an alkaline solution like the blood the chlorate of potassium is practically as stable and inert as the chloride, or as common salt.

In these remarks the writer disclaims the idea of censuring the members of the medical profession, because these are chemical subjects, and if blame be due anywhere it must undoubtedly fall upon chemists for neglecting to point out to the members of an allied profession the absurdities involved in these two cases.

There is, however, one great consolation for the uric acid and pyæmia patients who have been wrongly treated, viz., that both lithia water and chlorate of potash are (so far as we know) harmless, quite unlike the copious bloodletting and salivation treatments of a by-gone age.

At the same time it must be remembered that the use of valueless "remedies," however harmless in themselves, hinders or altogether prevents the search for real and rational ones. The sooner, therefore, attention is drawn to them the better for the patients, even should there be nothing to propose in lieu of those discarded.

Although the absurdity of the lithia water "bull" merely requires to be mentioned to a trained chemist to be at once recognised, it may be as well to give a few details.

In the first place, the substitution of lithium for sodium in the animal economy would probably be by no means an unimportant change. Physiologists have found that the substitution of the blood of one animal for that of another is possible in the case of allied species, but in that of animals belonging to different genera the change may be followed by immediate death. In all probability, therefore, it would be a very risky proceeding to convert the albuminate of sodium in human blood into albuminate of lithium, even if it were possible. Fortunately for the patient, however, this is as likely to be successful as the notion regarding the medicinal use of free phosphorus, viz., "the brain contains free phosphorus, and the more brain-work the more of that element is excreted. Therefore, to restore brain waste, give phosphorus pills." Such a crudity as this would be scouted, even as regards the mineral kingdom, *e.g.*, in the simple—or comparatively simple—operations of metallurgy.

In the second place, the question of quantity may be considered. As a bottle of lithia water contains about 5 grains of lithia, it is chemically equivalent to about 10 grains of soda.

The quantity of blood in an adult being about 100,000 grains, and containing about 294 grains of chloride of sodium, equivalent to about 156 grains of soda, it would evidently require 15 or 16 bottles of lithia water to replace the soda by lithia, supposing that sodium salts were absent from the food.

From the quantity and composition of the urine, however, we know that about 140 grains of common salt, equivalent to about 75 grains of soda, are excreted every twenty-four hours, derived, of course, from the food. It follows, therefore, that from 7 to 8 bottles of lithia water would be required every day for the sole purpose of dealing with the sodium salts introduced in the food.

These results are conclusive as to the value of the present practice.

To the chemist, however, the above figures are superfluous. He knows that the tendency is towards the formation of the more insoluble, not of the more soluble, compounds; and that for lithia to be of any service in avoiding deposition of urates in the joints or bladder, all bases which form compounds with uric acid of less solubility than lithic urate (potassium, sodium, ammonium) must be absent.

If we have a solution containing a phosphate, a magnesium salt, and free ammonia, we know that in a longer or shorter time a precipitate of ammonio-magnesic phosphate will take place, and the only way to prevent it is to ensure the absence of one of the constituents of the precipitate. We cannot argue "phosphate of potassium is more soluble than ammonio-magnesic phosphate, so by adding a salt of potassium to the solution we shall prevent the formation of the very sparingly soluble magnesium compound," and yet that is the assumption with regard to the medicinal use of lithia water.

It is a chemical exemplification of the truth of the old proverb about one man being able to lead a horse to the water, &c. It would be extremely convenient as regards uric acid patients if lithia water could be made to act in this way, but the laws of chemical combination do not admit of it. The medical profession, therefore, must recognise the fact, and seek elsewhere for a remedy or palliative for their patients.

An analogous case occurred in the gas world, where gas engineers strove for many years to purify the gas from bisulphide of carbon vapour by means of sulphide of calcium; and, *at the same time*, endeavoured to make the spent lime inodorous by converting it into carbonate before taking it out of the purifier. Here, again, it would have been very convenient if carbonate of calcium could have been induced to combine with carbon bisulphide, but it is hardly necessary to remark that the attempt was a failure.

Although it is a matter for regret that the science of therapeutics should be in such an elementary stage in the Nineteenth Century, still the physician is but in the same predicament as the chemist whose work lies in the vegetable or animal kingdoms. Take, for example, the apparently simple question of water analysis. The intellect of the civilised world for fifty years or more has been unable to devise a process (physical, chemical, microscopical, or biological) which will enable the operator to say with certainty, "This water is wholesome." There are several processes which are capable of detecting a bad water, but in many cases this can be done by the senses alone, and so recourse must be had to indirect methods, such as ascertaining the mortality and sickness amongst the people who use the water, or examining the source as to the probabilities of pollution. Little wonder, then, that medical science is frequently baffled in the attempt to deal with the complex problems of human pathology. Mineral analysis is but child's play compared with the study of morbid actions taking place in closed vessels, suspended in another closed vessel, the walls of all of them being opaque.

ON THE

CONSTITUTION OF THE ACID AMIDES.

By J. B. COHEN, Ph.D., Yorkshire College.

Formation of the Acid Amides.—These compounds are usually obtained by three methods, to which the following equations are assigned:—

1. $R \text{ or } H \cdot NH_2 + R \text{ or } H \cdot CO_2H =$
$= R \text{ or } H \cdot NH \cdot CO \cdot R \text{ or } H + H_2O.$

2. $R \text{ or } H \cdot NH_2 + R \cdot COCl =$
$= R \text{ or } H \cdot NH \cdot CO \cdot R + HCl.$

3. $R \text{ or } H \cdot NH_2 + R \text{ or } H \cdot CO_2R =$
$= R \text{ or } H \cdot NH \cdot CO \cdot R \text{ or } H + R \cdot OH.$

In 2 and 3 the mode of formation would point to the following constitution for the acid amides, which until recently has been generally accepted:—

$$\begin{array}{l} R \text{ or } H \cdot NH \\ \quad\quad | \\ R \text{ or } H \cdot C : O \end{array}$$

Carbonyl formula.

The first equation might be construed so as to yield a body of the constitution—

$$\begin{array}{l} R \text{ or } H \cdot N \\ \quad\quad \| \\ R \text{ or } H \cdot C \cdot OH \end{array}$$

Hydroxyl formula.

Derivatives of this class have actually been obtained by Pinner and others, and termed imido-ethers, and are therefore isomeric with derivatives of the substances having the first formula:—

$$\begin{array}{l} H \cdot N \\ \quad\quad \| \\ R' \cdot C \cdot OR \end{array}$$

Imido ether.

$$\begin{array}{l} H \cdot N \cdot R \\ \quad\quad | \\ R' \cdot C : O \end{array}$$

Alkyl amide.

Evidence upon which the choice of formula of the acid amide itself rests is of a very unsatisfactory kind.

The action of conc. HCl, conc. NaOH, PCl_5, P_2O_5, or Br would satisfy either formula.

One reaction appears definitely in favour of the *carbonyl* formula, whereas there are two which point equally to the *hydroxyl* formula.

Caustic soda and sodium ethylate unite with a few acid amides to form Na derivatives, in which the Na may be replaced by an alkyl group by the action of alkyl iodide, yielding compounds in which the new group is undoubtedly attached to the N atom.

$$\begin{array}{l} H' \cdot N \cdot R' \\ \quad\quad | \\ R' \cdot C : O \end{array}$$

On the other hand many acid amides unite with silver oxide to form silver compounds in which one atom of H is replaced by Ag, and these bodies treated with alkyl iodide yield the isomeric imido-ethers.

Beckmann's reaction, which consists in a molecular change produced by PCl_5 and other reagents on ketoximes forming isomeric acid amides, points at least to the intermediate formation of a compound of the *hydroxyl* formula.

Since working on the aromatic amides, it has frequently struck me as curious that of the series formanilide, acetanilide, &c., including benzanilide and oxanilide, the first—formanilide—should possess chemical and physical properties so totally different from the others of the series.

Formanilide crystallises in long prisms from alcohol, whereas the others, including benzanilide, form glistening plates all so similar in appearance that it would be impossible to identify them by their exterior alone. Formanilide, of which the formula is usually written—

$$C_6H_5NH \cdot COH,$$

yields with NaOH and Ag_2O, Na and Ag compounds, which none other of the series do. This evidently points to a fundamental difference in constitution.

Recent Views on the Constitution of the Acid Amides.—Tafel and Enoch showed that the Ag compound of benzamide differs from the Na compound by the fact that by the action of alkyl iodides the former yielded the imido-ether and the latter the isomeric alkyl amide thus:—

1. $$\begin{array}{l} C_6H_5 \cdot C \cdot OAg \\ \quad\quad \| \\ \quad\quad NH \end{array} + IC_2H_5 = \begin{array}{l} C_6H_5 \cdot C \cdot OC_2H_5 \\ \quad\quad\quad\quad \| \\ \quad\quad\quad\quad NH \end{array} + AgI$$

2. $$\begin{array}{l} C_6H_5 \cdot C \cdot N \cdot Na \\ \quad\quad \| \\ \quad\quad O \end{array} + IC_2H_5 = \begin{array}{l} C_6H_5 \cdot C \cdot N \cdot C_2H_5 \\ \quad\quad\quad\quad \| \\ \quad\quad\quad\quad O \end{array} + NaI$$

and Comstock shortly afterwards showed that similar reactions occurred in the case of formanilide. Formanilide was therefore regarded as an example of tautomerism; a view which is now generally held in regard to the constitution of the acid amides.

Leaving for the present the consideration of the Na compounds of the amides, I will take the larger class of acid amides in which an atom of hydrogen is replaceable by an atom of Ag.

The following (three of which were previously known) form Ag compounds, and the solids crystallise in needles or prisms.

$H \cdot CO \cdot NH Ag$	Formamide.
$CH_3 \cdot CO \cdot NH Ag$	Acetamide.
$CH_3 \cdot CO \cdot N(CH_3) Ag$	Methyl acetamide.
$CH_3 \cdot CO \cdot N(C_2H_5) Ag$. . . .	Ethyl acetamide.
$H \cdot CO \cdot N(C_6H_5) Ag$. . . .	Formanilide.
$C_6H_5 \cdot CO \cdot NH Ag$	Benzamide.
$C_6H_5 \cdot CO \cdot N(C_2H_5) Ag$. . . .	Ethyl benzamide.

The following do not form Ag compounds and crystallise in plates:—

$CH_3 \cdot CO \cdot N(C_6H_5)H$	Acetanilide.
$C_2H_5 \cdot CO \cdot N(C_6H_5)H$	Propionanilide.
$C_3H_7 \cdot CO \cdot N(C_6H_5)H$	Butyranilide.
$C_6H_5 \cdot CO \cdot N(C_6H_5)H$	Benzanilide.
$(C_6H_5)HN \cdot CO \cdot CO \cdot N(C_6H_5)H$.	Oxanilide.

In order to account for the different properties of the two groups, we must fall back upon Hantzsch's researches on the stereo-isomerism of the nitrogen compounds.

Hantzsch's Theory.—Hantzsch has shown that bodies of the following general formulæ exist in two modifications:—

	Anti.	Syn.
1. Aldoximes	$R'CH$ $\|$ $N \cdot OH$	$R'C \cdot H$ $\|$ $HO \cdot N$
2. Ketoximes	$R' \cdot C \cdot R''$ $\|$ $N \cdot OH$	$R' \cdot C \cdot R''$ $\|$ $HO \cdot N$
3. Diazobenzenes. . .	$R' \cdot N$ $\|$ $N \cdot OH$	$R' \cdot N$ $\|$ $HO \cdot N$
4. Diazoamidobenzenes.	$R' \cdot N$ $\|$ $N \cdot NHR'$	$R' \cdot N$ $\|$ $R'HN \cdot N$

The two modifications vary in stability according to the relative attraction of the groups.

The following is the order of attraction of various radicals for the OH group, according to Hantsch:—

$$CO_2H \cdot CH_2;\ CO_2H;\ C_6H_5;\ C_6H_4X;\ C_4H_3S;\ C_nH_{2n+1};\ CH_3.$$

* A Paper read before the British Association, Oxford Meeting Section B.

The first attract and the last repel. The group C_6H_5 also repels HNR'.

This attraction may be reversed in certain of the metallic compounds of the first three groups, and by the action of a metallic oxide the one configuration is converted into the second more stable one.

Thus NaOH or Na_2CO_3 convert—

$C_6H_5C.H$ into $C_6H_5C.H$
$\|$ $\|$
$HO.N$ $N.OM'$

$C_6H_5C.CH_3$ „ $C_6H_5C.CH_3$
$\|$ $\|$
$HO.N$ $N.OM'$

$C_6H_5.N$ „ C_6H_5N
$\|$ $\|$
$HO.N$ $N.OM'$

Application of the Theory to the Acid Amides.—Suppose we reverse the configurations 1 and 2, we get a formula which is capable of forming two configurations:—

Syn.	Anti.
R'N	R'N
‖	‖
HO.C.H	HC.OH
R'N	R'N
‖	‖
HO.C.R^2	R^2.C.OH

These formulæ will fully account for the constitution of the acid amides.

Before proceeding to apply the theory, I will assume that the acid amides, which form Ag compound and crystallise in prisms, belong to the "anti," and those which do not, belong to the "syn" configuration, and crystallise in plates. We can now predict which of the acid amides belong to the former class and which to the latter group.

1. All the acid amides derived from ammonia or fatty amines must be "anti" compounds of the general formula—

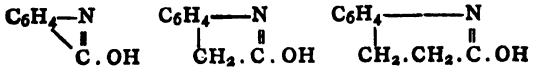
H or $C_n H_{2n+1}N$
‖
H or $C_n H_{2n+1}$ or $C_6H_5.C.OH$.

2. Bodies derived from aromatic amines must have the "syn" configuration:—

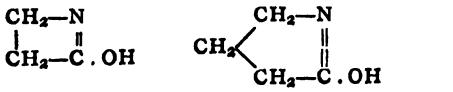
C_6H_5N
‖
$HO.C.H$ or $C_n H_{2n+1}$ or C_6H_5, &c.

Formanilide forms the only exception. This substance should belong to group 2, but evidently belongs to group 1. The other modification, which should be easily obtainable, will crystallise in plates, and will not form a Ag compound without reversal into the "anti" form.

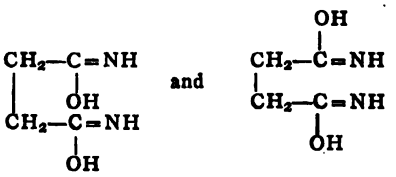
In anthranil, oxindol, and hydrocarbostyril, we have inner acid amides corresponding to the first three anilides. In these compounds it is obvious that the hydroxyl group must occupy the anti-configuration, and should unite with silver oxide and crystallise in prisms. This is the case, although in anthranil the Ag compound rapidly undergoes reduction:—



The same principle may be applied to the closed chains in the fatty compounds, which should give stable Ag compounds:—



It also accounts for cases of isomerism, such as the two succinamides which will probably have the configurations—



Formation of the Sodium Compounds.—In the course of numerous attempts to prepare pure Na acetanilide, one experiment gave an unexpected result, and it appears to me not only to bear out the above view of the constitution of these bodies, but to throw some light on the formation of the sodium compounds.

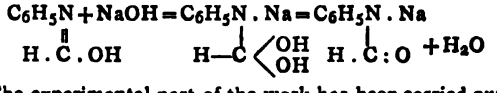
If acetanilide is dissolved in dry ether, and one molecule of solid sodium methylate is added, the liquid becomes turbid, and a compound of the formula—

$C_6H_5N:C(OH)CH_3.CH_3ONa$

separates out in needles. The two molecules are very loosely attached, and the acetanilide may be easily dissolved out from the other substance. The formation of this compound points to the following:—

1. Acetanilide is an unsaturated compound.

2. The formation of the sodium compounds in the case of anti compounds is preceded by the formation of addition compounds, with subsequent loss of one molecule of water, thus:—



The experimental part of the work has been carried out in conjunction with Mr. Archdeacon, and will shortly be communicated to the Chemical Society.

ESTIMATION OF UREA.

By WALTER COLQUHOUN, M.A.

In the CHEMICAL NEWS (vol: lxvii., p. 123) I described a method of estimating urea by hypobromite in which corrections for temperature, pressure, and tension of aqueous vapour were made by varying the amount of fluid taken, and I gave tables for the amounts to be taken at the various temperatures and pressures, within probable limits, in order that each c.c. of N evolved might represent 1 grm. of urea per litre in the fluid examined. The tables were calculated, after experiment, for an evolution of 92 per cent of N. After the paper had been printed, I noticed that, owing to the coincidence that the differences for every 5° F. practically correspond to those for 10 m.m. pressure, and are almost constant to three places, the results were given correct to two places of decimals, or hundredths of 1 c.c., by the empirical formula—

$$N = 2{\cdot}716 + \left(\frac{60-T}{5} + \frac{P-760}{10}\right) \times 0{\cdot}036;$$

where N = number of c.c. to be taken;
T = temperature Fahrenheit;
P = pressure in millimetres.

In the apparatus which I described an ordinary burette graduated from the stopcock in c.c.'s and tenths, was employed to measure the gas evolved; and a pipette graduated from 5 to 6 c.c. on the stem, to measure the fluid to be examined. For the sake of accuracy, double the quantity of fluid given by the tables was employed, so that every 2 c.c. of N evolved represented 1 part of urea per 1000. I would like to draw the attention of

those who devise or supply the many forms of apparatus for the estimation of urea to the advantages of this method.

1. The amount of fluid to be taken can be calculated in a moment from the empirical formula.

2. Instead of an apparatus of special graduation, the ordinary gas burette can be employed and tested as to accuracy against the pipette. If double the quantity of fluid given by the formula be employed, and the burette be graduated to tenths of 1 c.c., each division corresponds to 0·05 grm. of urea per litre, or, to put it in another way, there are 400 divisions to estimate a 2 per cent solution where many of the forms of apparatus have only 20.

3. The results are given corrected for temperature, pressure, and tension of aqueous vapour.

In my paper I pointed out that neglect of the proper corrections may lead at extreme probable temperatures and pressures to errors of from 0·2 to 0·23 per cent of urea on a 2 per cent solution; or, in other words, to 10 or 11 per cent of the reading.

Some forms of apparatus supplied use 1 c.c. of urine. The impropriety of taking such an amount does not require to be pointed out to chemists. Experiments with the weighing bottle have shown me—

1. That few 1 c.c. pipettes deliver 1 c.c.; the error sometimes amounting to 8 per cent.
2. That, even with the utmost care to use the pipette in the same way for each delivery, the amounts delivered may vary about 2 per cent.
3. That, using the pipette in the various ways which one commonly sees employed, the amounts delivered vary up to about 6 per cent.

If we add this error of 6 per cent of the reading to the possible error of 10 per cent through neglect of correction for temperature, &c., we arrive at results which are rather rough even for the unskilled.

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REDUCTION OF ALUMINA AND THE REFRACTORY EARTHS BY MEANS OF HYDROGEN.

By H. N. WARREN, Research Analyst.

The refractory earths alumina, glucina, chromium oxide, &c., have hitherto refused to become reduced by means of hydrogen. The author has lately, however, succeeded in reducing not only the above-named earths, but even zirconia, although silica and magnesia have as yet yielded no metal when exposed to the action of hydrogen gas. The difficulty in obtaining a substance free from carbon, and, at the same time, one of difficult fusibility, has naturally been the chief drawback in reducing the oxides in quantity, but in several instances distinct globules of melted metal have been obtained. The apparatus made use of consisted of a thin tube composed of compressed lime of excellent quality, the alumina enclosed therein being obtained by calcination of the aqueous chloride.

To one extremity of the tube was attached an apparatus for evolving pure and dry hydrogen gas, whilst to the exterior of the tube and upon the same spot wherein was enclosed the alumina, was allowed to impinge the flame from a powerful oxyhydrogen blowpipe, both gases being under the same pressure. At the same time a slow current of hydrogen gas was sent through the tube for about ten minutes. The action of the melted alumina upon the lime very soon, however, determined the destruction of the calcareous lining, owing to the increased fusibility of the compound formed, whilst its interior showed no trace of metallic formation. This, on referring to the action of hydrogen upon zinc oxide, will be better understood, a slow current of gas producing no effect; while, on the contrary, a swift current of gas readily reduces the oxide, through depriving the interior of the apparatus of the aqueous vapour formed, thus preventing re-oxidation of the metal under formation. A second tube, arranged as in the former case, was therefore experimented upon, using a brisk current of hydrogen gas. The interior of the tube upon examination now contained distinct traces of metal, perfectly bright, which in a further experiment distinct beads of aluminium were detached and examined, resulting in pure metal.

A mixture of Al_2O_3+CuO readily reduced to aluminium bronze, and tungsten and molybdenum were reduced and fused. Zirconia has as yet not afforded such striking results; whilst silica and magnesia have failed altogether.

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ON THE PREPARATION OF POTASSIO-MERCURIC IODIDE.

By E. G. CLAYTON.

Perhaps the most convenient way of preparing this salt, $2(KI,HgI_2),3H_2O$, is to concentrate ordinary Nessler's reagent, and subsequently to leave the solution to stand for some days. There is an abundant yield of the well-known fine yellow prisms, decomposable by water with the separation of mercuric iodide. The supernatant liquid is poured off, and the crystals may be superficially washed with strong alcohol and dried.

The writer, who tried this method in 1881, has never seen any reference to it, and thinks that, as merely requiring the use of a reagent already at hand in every laboratory, it is somewhat less troublesome than the similar, though not identical, processes usually described.

NOTE ON THE DETERMINATION OF SILICA IN BLAST-FURNACE SLAG.*

By P. W. SHIMER, Easton, Pa.

The object of this note is to call attention very briefly to the influence of spinel on the determination of silica in blast furnace slags. When fluxing aluminous ores with magnesian limestone, spinel is very apt to be found in the slag, especially when the slag is basic, the alumina in this case acting as an acid and combining with part of the magnesia to form magnesium aluminate. In the determination of silica in such a slag by the method of fusion with alkaline carbonate, the spinel seems to be almost wholly unattacked by the fusion and subsequent evaporation with hydrochloric acid, and is weighed with the silica at the end of the determination. In the case of one slag, the silica, before purification, was 34·25 per cent; after purification with sulphuric and hydrofluoric acids, it was found to be 31·52 per cent. The bluish-coloured residue left after the sulphuric and hydrofluoric acid treatment was found to dissolve easily in fused potassium bisulphate, and contained alumina and magnesia in the proportions necessary to form spinel. In the case of another slag, the silica, before separation of spinel, was 39·23 per cent; after separation, 34·73 per cent.

The points it is desired to bring out are, that spinel is not decomposed by the usual alkaline carbonate fusion, and therefore that it is never safe to omit the treatment

* From the *Journal of the American Chemical Society*, July, 1894. Read before the Lehigh Valley Section, May 3rd, 1894.

of the silica with sulphuric and hydrofluoric acid. All the slags in which spinel was found were stony slags, and therefore had the usual time in which to cool and crystallise. It is quite possible that, if the same samples had been chilled, the elements of the spinel would have remained in decomposable combination with the silica. However, even in the case of chilled samples, the possible presence of minute crystals of spinel should not be ignored, especially in basic slags rich in alumina and magnesia. By successive and repeated treatment of 100 grms. of a powdered spinel slag with hydrochloric and hydrofluoric acids, and boiling solution of sodium carbonate in a platinum dish, it was found to be possible to separate 1 grm. of microscopic crystals of spinel quite free from all impurities.

ON THE PHOTOGRAPHY OF THE BUNSEN FLAME REACTIONS IN THE ULTRA-VIOLET SPECTRUM.

By J. M. EDER and E. VALENTA.

In order to obtain sufficiently permanent spectra, the authors have constructed an apparatus consisting essentially of a wheel, the axle of which is inclined at 45° to the perpendicular, and which is kept by clock-work in slow rotation. At the edge of the wheel there is a broad stripe of very fine gauze of platinum wire, which on one side extends into a capsule containing the required saline solution, and on the other into the Bunsen flame. The slow motion conveys continually new liquid into the flame, which is thus kept constant. Care must be taken that only the upper part of the Bunsen flame is placed in front of the slit of the spectroscope, as it is free from the Swan spectrum.

The results of photographing the spectra of the flames of potassium, sodium, lithium, calcium, barium, and strontium salts which required in part an exposure up to thirty hours are appended to the memoir in very fine photographs. The ultra-violet spectrum of the green flame of boric acid has been examined in a similar manner.—*Weiner Akademie*, lx., p. 12, and *Zeit. Physik. Chemie*, xiv., p. 557.

THE WESTPHAL BALANCE FOR WAXES AND RESINS.

By J. F. LIVERSEEGE, F.I.C.

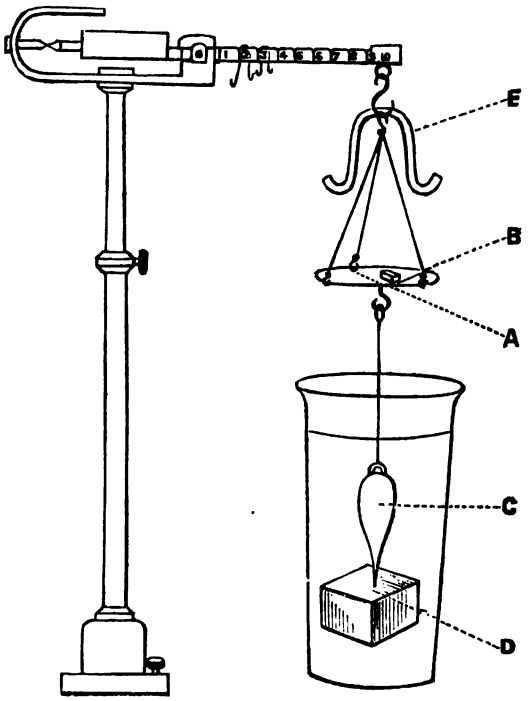
Having to take the specific gravity of a number of beeswaxes I found they might readily be determined by the Westphal specific gravity balance.

The thermometer plummet was replaced by a light scale pan, A, with a hook underneath to which was attached a spindle-shaped brass sinker, C, by means of a thin platinum wire. (The brass sinker was satisfactorily made for me by Mr. George, 36, Cambridge Street, Birmingham). In taking a specific gravity, the sinker is immersed in a beaker of distilled water about 60° F., the 1·0 rider, E, is put on the hook, a piece of lead, B, put in the pan to about restore equilibrium, and the adjustment finished by the screw. I found the thermometer plummet weighed about 20 grms, the brass sinker was 7 grms., the 1·0 rider 6½ grms., leaving about 7 grms. for the pan and the lead counterpoise.

A cube of wax, D, weighing less than 6½ grms. was cut smooth and the edges and corners cut off with a sharp knife, then polished with a duster, to prevent air bubbles sticking to the wax. This cube was put on the pan and the weights adjusted to restore equilibrium, and then read. The brass sinker was stuck into the wax and lowered into the water, air bubbles being brushed off, and the riders again adjusted and read. A genuine beeswax gave for the first reading 0·2615. Then 1 − 0·2615 = 0·7385 was the weight of the wax. The second reading was 1·0240, and 1·0240 − 0·2615 = 0·7625 is loss of weight or volume of wax,

$$\text{and specific gravity} = \frac{\text{weight}}{\text{volume}} \text{ or } \frac{0{\cdot}7385}{0{\cdot}7625} = 0{\cdot}968.$$

As specific gravity is relative there is no necessity to convert the specific gravity weight (of which 1·0 = 6·48 grms.) into absolute units.



If the solid is heavier than water, as resin, it may be determined in exactly the same way, but if necessary the point of the sinker is heated before sticking into the wax, &c., and allowed to cool before putting into the water.

Thus with resin the first reading was 0·406, and the second 0·957, and specific gravity =

$$\frac{1{\cdot}000 - 0{\cdot}406}{0{\cdot}957 - 0{\cdot}406} = 1{\cdot}078.$$

If there are air spaces in the interior of the wax, &c., it is melted in a small porcelain dish, allowed to cool spontaneously, and the cube cut when cold.

On Carbonic Hydrate, and the Composition of the Hydrates of Gases. — P. Villard. — Carbonic hydrate, discovered by Wroblewski, presents the greatest resemblance to hydrated nitrous oxide. These compounds are destroyed at the maximum tension of the gas at the temperature of +10 to +12, and are obtained under the same conditions. Their formation is accompanied with phenomena reminding us of superfusion, and which appear constant for substances of this kind. Their crystalline form is the same, and they are optically inactive. The composition of carbonic hydrate is $CO_2,6H_2O$, that of hydrated nitrous oxide being $N_2O,6H_2O$. Their formation heats are the same, 15·0 cal. for 1 mol., setting out with the free gas and liquid water.—*C. R.*, cxix., No. 6.

LONDON WATER SUPPLY.

Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending July 31st, 1894.

By WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To Major-General A. De Courcy Scott, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, August 9th, 1894.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 156 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from July 1st to July 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 156 samples examined one was recorded as "slightly turbid," and five "clear, but dull," the remainder being clear, bright, and well filtered. These were all from the mains of the East London Company. This Company has just finished laying 4200 yards of new 24-inch main near the spot whence the samples have been drawn. The disturbance thereby caused is amply sufficient to account for a slight turbidity in some of the samples. The suspended matter consists of ferruginous and clayey particles of a harmless character.

In the last monthly report for June we recorded an excess of 0·58 inch of rain over the average. July has been a still wetter month, the rainfall having been 3·27 inches—an excess of 0·89 inch over the 25 years' average of 2·38 inches.

There is very little change in the quality of the water, the constituents remaining almost identical in quantity with those in the June waters, and also in the water for the corresponding month of July last year.

Owing to an unexpected coincidence between the results of analyses of two of the waters, and the repetition of this coincidence for several months past, the conviction has been forced upon us that the samples of water collected for us and presumed to be respectively from the New River and Chelsea mains, were, through some systematic error, really the same water. This has now been confirmed by tracing the origin of the samples, which turn out to have been drawn from standpipes, supposed to be supplied by the different companies, but really both supplied by the New River Company. Steps have now been taken which will render such a mistake impossible in the future. Although this erroneous labelling is most unfortunate, it is not altogether to be regretted, as it explains the apparent discrepancy between Dr. Frankland's and our figures in regard to these two supplies, and moreover it gives, indirectly, a confirmatory proof of the extreme accuracy to which water analysis has been brought, and the complete trustworthiness of our own analytical results.

We are, Sir,
Your obedient Servants,

William Crookes.
James Dewar.

NOTES ON WATER ANALYSIS.

By C. A. SEYLER, B.Sc.

(Continued from p. 83).

II. *Carbonic Acid.*

In forming a judgment the analyst cannot afford to neglect the estimation of any substance which can throw light on the past history of the water. Carbonic acid is pre-eminently such a body. All waters come in contact with it in amount and form varying with their history, in small quantities in the atmosphere, in larger amount in the ground-air, and as carbonates during subsequent percolation. Being the characteristic product of the oxidation of organic matter, it is surprising, as Wanklyn points out, that it should have been so much neglected. The reason probably lies in the difficulty and uncertainty of the methods hitherto employed to estimate it, especially the gasometric ones. The introduction of special indicators for volumetric analysis has led to easy methods of estimating it in its various forms, and these have been systematically employed at this Institute for nearly two years with encouraging results.

A word on nomenclature is necessary. Carbonic acid may exist in water in three states—as carbonates, bicarbonates, and free acid. The usual German nomenclature is "combined" or "fixed" for that existing as simple carbonates, "half-bound" for that necessary to convert the carbonates into bicarbonates, and "free" for that remaining in excess. The elder usage of the term "free carbonic acid" for the sum of the "half-bound" and "free" is very objectionable, as concealing important differences. It is that estimated by Pettenkofer's method, and being approximately that expelled on boiling, might be termed the "volatile" CO_2, as contrasted with the "fixed." Thus we have the following scheme:—

$$\text{Total } CO_2 < \begin{matrix}\text{fixed}\\ \text{volatile} < \begin{matrix}\text{half-bound.}\\ \text{free.}\end{matrix}\end{matrix}$$

The volumetric methods are based on the following facts:—

1. Methyl orange is unaffected by CO_2, and hence the bases present as carbonates or bicarbonates can be at once titrated by standard acid, whether excess of CO_2 be present or not. $Na_2CO_3 + 2HCl = 2NaCl + H_2O + CO_2$.

2. Carbonates are alkaline to phenolphthalein, bicarbonates neutral, free CO_2 acid. Hence (*a*) a carbonate titrated with acid under conditions which prevent loss of CO_2 (in dilute solution) becomes neutral when all the carbonate is converted into bicarbonate.

$$Na_2CO_3 + HCl = NaHCO_3 + NaCl.$$

Neutrality is reached with half the acid required with methyl orange. (*b*) Free carbonic acid in dilute solution can be titrated with either sodic carbonate or hydrate, neutrality arriving when the alkali is converted into bicarbonate.

1. $CO_2 + NaOH = NaHCO_3$.
2. $CO_2 + H_2O + Na_2CO_3 = 2NaHCO_3$.

With equivalent standard solutions twice the amount of sodic carbonate as of hydrate is required to neutralise the CO_2. These fundamental facts have been repeatedly verified on alkaline carbonates, and their applicability to water analysis depends on the similar behaviour of the sparingly soluble carbonates and bicarbonates of calcium and magnesium. The simple carbonates of calcium and magnesium are soluble to a slight extent in water free from CO_2, and their solutions are alkaline to phenolphthalein. This is verified by the following observations:—Every water with temporary hardness becomes alkaline to phenolphthalein upon boiling; such a reddening is no proof of the presence of an alkaline carbonate. Solutions of $CaCO_3$ and $MgCO_3$ in carbonic acid water were made; these both became alkaline to phenolphthalein upon boiling off

the CO_2, or upon simply blowing a current of air through them. The $CaCO_3$ in solution after boiling was determined by titration with methyl orange, and found to be about 3·4 m.grms. per 100 c.c. This agrees with Tiemann and Mylius and Foerster, and corresponds to a hardness of about 2·3°. $MgCO_3$ is still more soluble, and gives a very strongly alkaline solution. The neutrality of the bicarbonates is not as easy to prove as with sodium and potassium. The simplest way seems to be by double decomposition.

Lime being nearly as strong a base as soda,* if a calcium salt be mixed with sodic bicarbonate calcium bicarbonate will be formed, and if this is neutral the reaction will remain neutral. If strong solutions be mixed the bicarbonate is decomposed, $CaCO_3$ is precipitated, and the liquid becomes strongly acid to phenolphthalein. But if the solutions be so dilute that no precipitation occurs (as in natural waters), the reaction remains neutral. The following experiments show this, and give some idea of the amount of $CaCO_3$ which water can hold in solution as bicarbonate:—

1. A very rapid current of CO_2 with agitation re-dissolved nearly the whole of the $CaCO_3$ precipitated from lime-water (equivalent to 205 m.grms. per 100 c.c.). The filtered solution contained 197·5 m.grms. This deposited much $CaCO_3$ even in a few hours in a closed vessel.

2. A slower current did not completely re-dissolve the $CaCO_3$. The solution contained (*a*) 100 m.grms., (*b*) 112 m.grms.

3. Lime-water was added to solution of CO_2 till precipitate no longer dissolved. The filtered solution contained 110 m.grms.

These solutions on standing a night in closed or open vessel deposited much $CaCO_3$, and then contained respectively 65 and 63 m.grms. per 100 c.c. After many weeks in a stoppered vessel this became reduced further to about 32 m.grms., equivalent to a temporary hardness of about 21° (grains per gall.). This is rare in natural waters, and corresponds with the maximum I have met with.

In agreement with this are the following experiments:—Equivalent solutions of $CaCl_2$ and $NaHCO_3$ (both neutral to phenolphthalein) were mixed so as to produce a liquid of 40° temporary hardness. No precipitation occurred, and the solution was nearly neutral to phenolphthalein, requiring only a few drops of N/20 Na_2CO_3 to give a permanent pink. Weaker solutions of 8° and 4° were perfectly neutral, but stronger solutions (80°) became distinctly acid and soon precipitated. As is well known, even strong solutions of magnesium salts are not precipitated by alkaline bicarbonates. N/20 solutions when mixed remained clear and neutral. We may therefore conclude that solutions of calcium and magnesium bicarbonates are neutral to phenolphthalein.

From this fact we draw the following conclusions:—

1. If a water is neutral or acid to phenolphthalein (the commonest case), the "half-bound" CO_2 is equal to the fixed, and the "volatile" CO_2 (Pettenkofer) is equal to the sum of the fixed and free, *i.e.*, the sum of the two titrations.

2. If a water is alkaline to phenolphthalein it can contain no free CO_2, and the volatile CO_2 will be less than the fixed by an amount determined by titration with acid until neutral to phenolphthalein.

Practical Details.—The fixed CO_2 is determined by a simple titration with acid and methyl orange. The method was first suggested, I think, by Hehner, who used cochineal; Lunge suggested methyl orange, which is the most convenient. 100 c.c. of the water, 3 to 4 drops of the indicator (1 : 1000), and N/20 mineral acid will be found practical. 1 c.c. = 1·1 m.grm. CO_2 or 2·5 m.grms. $CaCO_3$.

When the alkalinity is very small methyl orange leaves it doubtful if there may not be a trace of acidity. In such cases lacmoid will decide, giving a blue colour with the least trace of a carbonate, and being only slightly affected by CO_2. In cases of very slight acidity or alkalinity (*e.g.*, in rain-water) I have found the method of Mylius and Foerster very useful. It is fully described in the CHEMICAL NEWS, lxiv., p. 229. The titrations with N/1000 solutions are quite practicable. The ethereal solution must be perfectly neutral, which is secured by shaking up with a little water and adding N/1000 Na_2CO_3 till a very faint pink appears in the aqueous liquid. Then pipette off the water, and add the liquid to be tested. The same ethereal solution may be used several times in this way. The combined CO_2 may be very prettily titrated by this process on 5 c.c. or less of the water, as shown by following experiments:—

100 c.c. water with methyl orange and N/20 acid required 6·6 c.c.; 5 c.c. water with erythrosin ether (daylight) required 16·2 c.c. N/1000 acid, = 6·48 c.c. N/20. By gaslight, using comparison cylinders, 16·3 c.c. N/1000. I find that *lacmoid* can be used in a similar way, the red lacmoid being soluble in ether and the blue insoluble. Used in this way 5 c.c. of above water required 16·3 c.c. N/1000 acid.

The determination of the *free* CO_2 is particularly valuable. The method is known on the Continent as Trillich's ("Die Muenchener Hochquellenleitung," 1890), but was also suggested by Leeds (*Journ. Am. Chem. Soc.*, 1891, 13). It consists of titrating with phenolphthalein and either sodic carbonate or hydrate. I can find no advantage in the latter; it keeps badly and is only half as delicate. Use 100 c.c. of the water, and not too little indicator, and run in the N/20 Na_2CO_3 till a faint pink is permanent. The colour vanishes rather slowly towards the end. 1 c.c. = 1·1 m.grm. CO_2. The titration must, for accurate results, be repeated, running in nearly the right amount at once and then finishing drop by drop. The sodic carbonate and acid used should be exactly equivalent, with methyl orange as indicator. In this case the free and combined CO_2 may be done upon the same 100 c.c., titrating first with the alkali and then adding methyl orange and titrating with acid. The number of c.c. of soda used is of course subtracted, and the results are quite accurate, unless the combined CO_2 be very small.

As free CO_2 is present, and we have thus determined the free and fixed CO_2, their sum is the volatile CO_2. Thus, taking 100 c.c. of water, if p = number of c.c. of N/20 soda carbonate used and m the number of c.c. of acid, we have—

Free CO_2	= 1·1 p	parts per 100,000
Fixed CO_2	= 1·1 m	,, ,,
Volatile CO_2	= 1·1 $(m+p)$	
Total CO_2..	= 1·1 $(2m+p)$	

If the water is alkaline to phenolphthalein (as sometimes happens in perfectly natural waters), 100 c.c. are titrated till the pink vanishes, and then finished with methyl orange.

If m be the number of c.c. of acid required with methyl orange, and p' that required with phenolphthalein, then we have—

Fixed CO_2	= 1·1 m	parts per 100,000
Volatile CO_2	= 1·1 $(m-2p')$	
Total CO_2	= 1·1 $(2m-2p')$	

(We have $2p'$ here because the same acid corresponds to twice as much CO_2 when phenolphthalein is used as when methyl orange is used).

Thus two simple titrations will in a few minutes give us complete information as to nature and amount of the carbonic acid existing in the water.

(To be continued.)

* Ostwald, "Outlines of Chemistry," III. Few waters containing calcium bicarbonate are devoid of sodium salts, and the final equilibrium is independent of the original distribution of the bases.

RECENT PUBLICATIONS RELATING TO CARBOHYDRATES.*

By W. E. STONE, Purdue University.

THESE notes are intended to include the more important contributions to the subject appearing in scientific journals in 1893. The term "carbohydrates" is used in its older and broader sense in order not to exclude a considerable number of bodies commonly sharing in the interest paid to the true carbohydrates.

Constitution.

Without doubt much light has been thrown upon the structure of the carbohydrates, from various standpoints. The formation of artificial glucosides between sugars and alcohols by Fischer (*a*) with the constitution of ethers is regarded by him as a significant support for the anhydride formula of dextrose as proposed by Tollens (*b*). Moreover, he regards the hexobioses (sucrose, &c.) as of similar ether-like constitution, composed of two glucose molecules. Another observer has noted that sodium glucosate does not form a compound with phenylhydrazin as it should do if glucose were an oxy-aldehyd, and this is also presented as a support for the Tollens formula (*c*).

The continued researches on cellulose by the English chemists Cross and Bevan, are apparently on the eve of yielding some definite knowledge of this very slightly understood body. They have been able to recognise in jute fibre several distinct radicles or groups which they believe to constitute a genetic series. In general they recognise *ligno-cellulose*, easily soluble in mild reagents; *oxy-cellulose*, which is more resistant; and, finally, cellulose proper. In one of the latter the methoxyl group, $O.CH_3$, could be recognised, and in another group, $C_{11}H_{10}O_4$, yielded furfurol. By chlorination a compound resembling quinone chloride was obtained. The oxy-cellulose was found to be susceptible of oxidation to a body which yielded furfurol, from which the authors infer that the production of furfurol from fibres does not necessarily indicate the presence of a pentose molecule (*d*).

Starch is regarded as a complex of glucose molecules, not differing in any essential in constitution from sucrose or maltose. It is considered as a higher and more complex form of sucrose, while dextrin is a type of maltose (*e*).

On the other hand, other investigators bring additional proof of the theory that starch is a complex which breaks down by successive subtractions of glucose molecules, the more or less complex residue constantly changing in its character. Five stages of this process are recognised:—(1) Amylo-dextrin, $(C_{12}H_{20}O_{10})_{54}$; (2) Erythro-dextrin, $(C_{12}H_{20}O_{10})_{18}$; (3) Achroo-dextrin, $(C_{12}H_{20}O_{10})_6$; (4) Isomaltose; and (5) Maltose, $C_{12}H_{22}O_{11}$ (*f*).

Syntheses.

Artificial glucosides have been prepared by Fischer by the action of gaseous hydrochloric acid upon solutions of different sugars in various alcohols. In some cases where the sugars are not soluble, the acetyl-compounds may be used. The reaction seems general, and the products resemble the natural glycosides, losing the characteristic properties of sugars towards Fehling's solution and phenylhydrazin, as well as the sweet taste. The compounds are decomposed by inverting and by heating with dilute acids. The reaction does not seem to take place between sugars and monovalent phenols. The following derivatives have been prepared:—Ethyl and methyl glucoside, ethyl and methyl rhamnoside, and ethyl and methyl arabinoside, benzoyl glucoside, and glycol glucoside (*g*).

The physical isomers of the synthetic *d*-heptose, *d*-heptonic acid and *d*-heptite, have now been prepared by similar methods from *l*-mannose, from which were obtained successively *l*-manno-heptonic acid, *l*-manno-heptose, and *l*-manno-heptite. These respectively, by combination with the corresponding *d*-mannose derivatives in molecular proportions, gave the inactive series (*h*).

Various derivatives and salts of the *d*-manno-heptonic acid have been prepared, and among other products, oxidation with nitric acid is found to yield the fourth pentoxy-pimelic acid (*i*).

Erythrite has been synthetically made from diacetin by preparing the bromine addition product and then treating with silver oxide. The product thus obtained possessed all the properties of natural erythrite (*j*).

Following Fischer's building up of the hexose molecules, Anton Whol has now accomplished the reverse, or building down ("*Abbau*") of a hexose to a pentose. Dextrose forms with hydroxylamine, glucosoxime. The pentacetyl derivative of this gives hydrocyanic acid when treated with caustic potash, leaving behind a pentacetyl pentose. From this the acetyl radicles were easily removed, and the remaining syrup revealed all the properties of a pentose. The specific rotation was $(\alpha)_D = -104°$, which showed it to be the stereoisomer of the ordinary or lævo-arabinose, from which Fischer built up lævo-dextrose. The author proposes to continue the process to the tetroses, and also examine other hexoses in the same way (*k*).

New Carbohydrates.

The discoveries in this field have not been notable. E. Merck has isolated from *Adonis vernalis* a body of the composition $C_5H_{12}O_5$, sweet, but optically inactive, and without action on Fehling's solution (*l*). This, on examination by Fischer, was found to be identical with the pentite derived from the ribose obtained from arabonic acid. This pentite, called *Adonite*, is the first to be found in nature (*m*).

Trehalum is a tasteless crystallinic substance obtained from trehal-manna after the removal of trehalose. Its formula is $C_{24}H_{42}O_{21}$. It is slightly soluble in water, $(\alpha)_D = +178{\cdot}2$, without action on Fehling's solution, forms no compound with phenylhydrazine, is unchanged by yeast or invertin, upon hydrolysis with acids forms dextrose (*n*).

From the mushroom, *Boletus edulis*, a gelatinous substance has been obtained, insoluble in alcohol, soluble in caustic potash, and by hydrolysis yielding dextrose. It was regarded as a modified form of cellulose and named *para-dextran* (*o*).

When chinovin is decomposed by means of hydrochloric acid there remains a body called *chinovit* which can be hydrolysed and yields a body called *chinovose*, which has been identified as isomeric with rhamnose and fucose, *i.e.*, is a methyl pentose. The chinovit is a glucoside, ethyl-chinovosid, corresponding to the artificial glucosides already mentioned (*p*).

Pentosans and Pentoses.

Pentosans have been found in solution in the juices of green plants in large variety. By an ingenious use of the aniline acetate reaction very minute quantities of furfurol as well as methyl furfurol could be distinguished. Experiments made in this connection showed that under the same conditions of distillation for furfurol, the hexoses never produced more than 0·2 per cent of that product. In general, the amount of pentosans in solution was greater in the morning than in the evening. A similar study of germinating seeds showed that their content of pentosans decreased and the proportions of the same in growing parts of the plant increased, as did also the total amount of pentosans. The author concludes that pentosans are assimilational products, existing in soluble form, undergoing translocation and change into insoluble forms, and again being dissolved and transported as the needs of the plant may require (*q*).

The occurrence of pentosans has been noted in cassava, of which they constitute 3·92 per cent of the dry matter (*r*).

* *Agricultural Science*, viii., No. 2.

Eleven kinds of natural gums reveal the presence of pentosans under the orcin reaction (*s*). In the fruit of *Gynocladus canadensis* a complex called gluco-araban has been noted which yielded glucose and arabinose (*t*), and a similar galacto-araban occurs in the seeds of *Lupinus luteus*, yielding galactose and arabinose (*u*). Pentosan (xylan) is extracted from straw by its treatment with quicklime in the manufacture of straw paper, and this alkaline liquor is a good source for xylose (*v*).

As a hydrolytic agent for the inversion of gums, and more particularly the pentosans, hydrochloric acid is recommended in preference to sulphuric acid, the formation of uncrystallisable products being thus avoided. The acid can be removed by neutralisation with lead carbonate (*w*).

Compounds of the pentoses with acetyl and benzoyl have been prepared. Analyses of the former show each of these sugars to contain four hydroxyl groups; the latter were of indefinite composition. Tetra-acetyl xylose, $(\alpha)_D = -25{\cdot}43°$. Tetra-acetyl arabinose, $(\alpha)_D = +26{\cdot}39°$ (*x*).

Authorities and Publications.

(*a*) E. Fischer, *Berichte der Chem. Gesell.*, xxvi., 2400.
(*b*) "Handbuch d. Kohlenhydrate," p. 10.
(*c*) L. Marchlewski, *Berichte d. Chem. Gesell.*, xxvi., 2928.
(*d*) Cross, Bevan, and Beadle, CHEM. NEWS, lxviii., 225 and 235.
(*e*) Scheibler and Mittelmeier, *Berichte d. Chem. Gesell.*, xxvi., 2930.
(*f*) Lintner and Düll, *Ibid.*, 2533.
(*g*) E. Fischer, *Ibid.*, 2400.
(*h*) W. W. Smith, *Annalen d. Chem.*, cclxxii., 182.
(*i*) G. Hartmann, *Ibid.*, 190.
(*j*) M. Griner, *Comptes Rendus*, cxvii., 553.
(*k*) A. Wohl, *Berichte d. Chem. Gesell.*, xxvi., 730.
(*l*) E. Merck, *Chem. Centralbl.*, 1893, i., 344.
(*m*) E. Fischer, *Berichte d. Chem. Gesell.*, xxvi., 633.
(*n*) Scheibler and Mittelmeier, *Ibid.*, 1331.
(*o*) E. Winterstein, *Ibid.*, 3098.
(*p*) E. Fischer and C. Liebermann, *Ibid.*, 2415.
(*q*) G. de Chalmot, *Am. Chem. Journal*, xv., 21, 276.
(*r*) Ewell and Wiley, *Ibid.*, 284.
(*s*) Guichard, *Bull. Soc. Chim. de Paris*, [3], ix., 19.
(*t*) Stone and Test, *Am. Chem. Journal*, xv., 660.
(*u*) E. Schulze, *Landw. Vers.-Stationen*, xli., 207.
(*v*) Stone and Test, *Am. Chem. Journal*, xv., 195.
(*w*) C. Councler, *Chem. Zeit.*, xvi., 1719.
(*x*) Stone, *Am. Chem. Journal*, xv., 653.

(To be continued).

NOTICES OF BOOKS.

The Physiology of the Carbohydrates; their Application as Food and Relation to Diabetes. By F. W. PAVY, M.D., LL.D., F.R.S., F.R.C.P., &c. London: J. and A. Churchill. 1894. 8vo., Pp. 289.

THE work before us is of great importance both from a theoretical and a practical point of view. Dr. Pavy undertakes the refutation of the glycogenic doctrine; that is, of the view that glycogen, $(C_6H_{10}O_5)n$, is a product from which is generated the sugar developed after death in the liver. It has been very generally held that sugar is produced in the liver, but from the researches of Dr. Pavy it follows that the liver, at the moment of death, does not contain an exceptional amount of sugar as compared, *e.g.*, with the muscles. It is now experimentally proved that the blood leaving the liver does not contain more sugar than that flowing to it. In accordance with the "glycogenic doctrine," it has been assumed that sugar disappears from the blood whilst passing through the systemic capillaries, but of this assumed fact there is no evidence. It appears that the liver, instead of throwing sugar into the general circulation, actually holds it back. But in a morbid condition this action ceases, and the result is diabetes.

Sugar in small proportion is present in the urine, as well as in the blood. In the former, the quantity in a healthy condition is about 0·5 per 1000. The absence of reaction with Fehling's test is no proof of the absolute absence of sugar. The quantity may be too small to be thus recognised, and other materials present may mask the reaction. Thus the ammonia liberated by the action of the potassa in the test upon the nitrogenous matter present may hold in solution the cuprous oxide present when small in quantity. Hence, before asserting the absence of sugar we must apply Brücke's test. The urine is treated with neutral, and then with basic, lead acetate. Uric, sulphuric, phosphoric, hydrochloric acids and other matters are thrown down in combination with lead, whilst the sugar is left in solution. The whole is filtered, and to the filtrate are added ammonia and more lead acetate. The precipitate is collected and well washed with distilled water. The sugar existing in the washed precipitate is then liberated by the prolonged action of a current of sulphuretted hydrogen. It is next filtered and heated to expel any excess of sulphuretted hydrogen. The residual liquid is concentrated by evaporation *in vacuo*. Treatment with purified animal charcoal follows, to remove colouring matter, and from the charcoal the sugar is recovered by thorough washing.

Diabetes, as the author shows, depends upon two conditions, an impaired power of stoppage in the patient, and the amount of carbohydrates ingested. The latter of these conditions only is under dietetic control. But in severe cases sugar may still be excreted, even when the patient is restricted to purely animal diet. This result is due to the facts that animal foods contain a small amount of free carbohydrates; and, secondly, that in the process of digestion sugar may be split off from the proteine compounds. If the carbohydrates are not disposed of in a normal manner, they escape from the system as waste, this escape being diabetes.

The author appears to have been successful in refuting the "glycogenic" doctrine, and has thus thrown a novel and welcome light into one of the darkest places of physiology.

Lessons in Organic Chemistry. Part I. Elementary. By G. S. TURPIN, M.A. (Camb.), D.Sc. (Lond.), Principal of the Technical School, Huddersfield. London and New York: Macmillan and Co. 1894.

THIS handy and well-arranged little book is adapted, according to the publishers' lists, to the elementary stage of the South Kensington syllabus.

In the instructions for ultimate organic analysis it is remarked that the determination of nitrogen by the Will and Varrentrapp process is now superseded by the Kjeldahl method.

For the determination of vapour densities the method of Victor Meyer is described as having almost totally superseded the procedures of Hofmann and of Dumas.

For determining the molecular weights of non-volatile substances, the apparatus of Beckmann is described and figured.

The "present regulations" for the denaturing of alcohol as sold duty free for industrial purposes, specify that "certain small proportions of wood-spirit and of *light petroleum* shall be employed as the methylating mixture." We strongly question whether this admixture will render the spirit "practically undrinkable," and we fear that the light petroleum will very seriously interfere with its manufacturing uses. The German Revenue regulations more practically allow of the use of a trace of Dippel's animal oil, which not even the most hardened

toper can swallow, and which, if used in the minimal proportion necessary, would not interfere with the industrial and scientific uses of the spirit.

A very important use of glycerin, its employment in the tinctorial arts, has been overlooked.

We are much pleased to notice the comparison (p. 122) between the sugar-cane and the sugar-beet. Supposing the same care applied the cultivation of each, the beet could not compete with the cane without heavy protective duties.

As far as this work has gone, it gives an exceptionally clear and intelligible oversight of the leading truths of organic chemistry.

The Mineral Industry: its Statistics, Technology, and Trade in the United States and other Countries from the Earliest Times to the End of 1893. Vol. II. Edited by Richard P. Rothwell. London and New York: Scientific Publishing Company. 1894.

The substances treated of in this valuable compilation are: Abrasive materials, alum, aluminium, antimony, arsenic, asbestos, asphaltum, baryta, bauxite, bismuth, borax, bromine, cadmium, cements, chemical industries in general, chrome ores, clays, coal, copper, copperas, cryolite, felspar, fluor-spar, gold and silver, graphite, gypsum, iodine, iron and steel, lead, limestone, marble and lime, lithographic stones, magnesite, magnesium, manganese, marls, mica, nickel, onyx, peat, petroleum, phosphates, phosphorus, precious stones, pyrites, quicksilver, rare elements, salt, slate, sodium, sulphur, talc and steatite, tin, tungsten, whetstones, and zinc.

Upon these items follows an account of the mineral production, imports, and exports from different countries.

Next come market reports, notices of mining schools in the United States and Canada, improvements in ore-dressing and quarrying, and a historical dissertation on the origin of ores.

There are also tables for the conversion of metric weights and measures into those used in the United States. The reader is not reminded that the measures for liquids customary in the United States are not identical with those employed in Britain. Against the latter we find in the preface the *banal* outburst of wrath. We can assure Mr. Rothwell that two causes alone have prevented the introduction of the metric system into Britain, which would have been effected long ago were it not for the polysyllabic nomenclature which was devised by the French originators of the system. Very drastic legislation would also be needed to force metric weights and measures in retail trade upon the public.

On examining the work before us we are at once convinced of its extraordinary value as an accurate summary of the world's mining industries and their products.

It may, perhaps, surprise the reader to find calcium, boron, silicon (!), and strontium classified as "rare elements" (p. 535). But the author has, with perhaps not unquestionable judgment, included here not merely the substances which are really rare, but also those which do not occur naturally in an elementary state.

It appears that the manufacture of aluminium—or aluminum, as the editor prefers to name it—by the Cowles process has been pronounced an infringement of the Hall process. The use of aluminium sulphate in the treatment of foul waters is duly recognised, though it is not yet used in some important cases here mentioned.

A very important application of asbestos has been successfully introduced, *i.e.*, for the manufacture of fire-proof ropes.

Arsenic is recommended for the destruction of Colorado beetles and locusts.

Under the head of "Cement" we find it stated that "in the past few years Germany has surpassed England in the quantity, and also, as is generally admitted, in the quality, of her product."

In the chapter on coal, we find little reference to the probable increased output from the beds of South Africa, and from those of China, which, if geologists are not mistaken, even exceed in importance those of the United States. Hence China may be the great industrial region of the future.

One feature of "The Mineral Industry" contributes less to its value and interest than to the cost of its production. The book is garnished with portraits not merely of the editor, but of the authors of its various sections. Still, in spite of this fantastic feature, "The Mineral Industry" is a work of wonderful value which deserves wide circulation.

Report of the Senior Analyst on the Analytical Laboratory and Agricultural and Mineralogical Museum, for 1893. Cape of Good Hope: Department of Lands, Mines, and Agriculture. Cape Town: W. A. Richards and Sons. 1894.

Since the last Report it has been found advisable to institute an official tariff of charges for the performance of analyses which have hitherto been done free. This change was made with the view of checking the large quantity of miscellaneous work which flooded the laboratory, and prevented the Department from carrying on original investigations and experiments. In order to avoid entering into competition with private analysts, on terms ruinous to the latter, it was decided that only farmers should have the benefit of a low fee, other persons having to pay on a higher scale. A list of charges is given, which vary from 5s. 3d. to £5 5s., according to the nature of the examination; 353 samples were analysed during the year 1893, gold quartz heading the list with 94; of these, 16 contained no gold, 29 only traces, while the remainder averaged only 14¼ grains per ton—results which must have been very disheartening for the prospectors. Of much more real importance to the Colony are the 62 analyses of soils. South Africa has been called the Land of Gold, Diamonds, and Ivory; but with her magnificent climate and her enormous tracts of fertile land, there is no reason why the Cape Colony should not become an important agricultural country. Nothing is so uncertain as mining; and it is, after all, extremely doubtful whether even successful mining does much good to the country when nearly all the shares are held abroad.

It is remarkable, and serious to note, that of 44 samples of so-called drinking water, sent from 16 different towns and settlements, 31 are described as *unfit for use*. Out of these 44 samples, 19 were from wells, but only 5 of these were found to be sufficiently pure for consumption; one was even described as *not fit even to wash clothes*. In a country where fever is so prevalent it is more than ever of importance that the water supply should be pure, and we earnestly hope the authorities will not neglect the serious warning they have received.

The Agricultural and Mineralogical Museum has been greatly improved during the year; much progress has been made with the cataloguing, and, moreover, a more careful arrangement and classification of the specimens has been completed.

Buletinul Societatii de Sciinte Fisice. (Bulletin of the Society of Physical Science). Edited by M. C. Istrati. Bucharest. February, 1894.

The editor of this journal has wisely taken the trouble to print it in French as well as in its native language, the left hand column only in each page being in Roumanian. The current number contains among other papers a biography of M. Béchamp, the distinguished Roumanian chemist. M. Béchamp is now 78 years of age, but is still full of vigour and work. There is also a long article on "Researches on Pyroxyline," which have been carried on in the laboratory of M. Friedel.

CORRESPONDENCE.

A SUPPOSED NEW GASEOUS ELEMENT IN THE ATMOSPHERE.

To the Editor of the Chemical News.

SIR,—You have been good enough to reprint in last week's CHEMICAL NEWS the two letters I addressed to the *Times* on the subject of the New Gaseous Element in the Atmosphere, the discovery of which was announced by Lord Rayleigh and Prof. Ramsay at the British Association Meeting at Oxford. When I wrote those letters, the sole information I had to go upon was the newspaper reports of the communication made to the Chemical Section. It appears now, however, that I was not conversant when I wrote with all the facts of the case. I observe that you had already examined, on behalf of the discoverers, the spectrum of the new body, and had come to the conclusion that "*the spectrum is a very definite and characteristic one.*" If the words "definite" and "characteristic" mean that the spectrum differs essentially from that of any recorded substance, then this result should go a long way to settle the elementary character of the new substance. It does not, however, touch the question which specially interests me as to whether the body is a normal constituent of the atmosphere. This doubt might be very simply dispersed. If air contains the new body, and nitrogen obtained from any chemical source (other than air) does not, then such nitrogen when it is subjected to the process used by Lord Rayleigh and Prof. Ramsay for the separation of the new gas, ought to yield *no* unabsorbable or uncombinable "inert gas" of the nature they have described. This simple experiment would settle, once for all, the suggestion that the new substance was being manufactured, and its apparent absence from liquid air must be otherwise explained.—I am, &c.,

JAMES DEWAR.

Royal Institution, Aug. 28, 1894.

OBITUARY.

DR. KARL HEUMANN.

THE German technical papers, especially the *Chemiker Zeitung*, notice the death of Professor Dr. Karl Heumann, of the Zurich Polytechnicum.

This distinguished chemist was lost to science at the early age of forty-three years, when he had just completed the second volume of his great work—"The Aniline Colours and their Manufacture" ("Die Anilin Farben und ihre Fabrikation"). His chief original memoirs were: "Contributions to the Theory of Luminous Flames," "On the Formation and Decomposition of Metallic Sulphides," "On the Ultramarine Compounds," "On the Synthesis of Indigo and the Allied Colouring-Matters."

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxix., No. 5, July 30, 1894.

The General Council of the Faculties of Lyon invites the Academy to send representatives to the inauguration of the Statue of Claude Bernard, which will take place at Lyon on October 28th next.

A Contribution to the Study of the Structure of Steels.—F. Osmond.—The author has examined a half hard steel (C, 0·45; Si, 0·07; S, 0·016; P, 0·036; Mn, 0·35); a hard steel (C, 1·24; Si, 0·35; S, 0·012; P, 0·017; Mn, strong traces); and manganese steel at 12 per cent. The facts observed have not all met with their explanation. The impossibility of isolating the various constituents of steel for analysis does not allow us to define them all with sufficient precision. Still for steels of medium hardness, which are the most important, the study of the structure furnishes often very precise information on the maximum temperature of heating, on the temperature at which it has been tempered, and the rate of cooling. It is always useful to record the observations photographically. A magnifying power of 800 diameters is often necessary and generally suffices for the details.

A Refractometer with a Trough capable of being Heated. Application to the Measurement of Fatty Substances.—M. Féry.—This paper cannot be intelligibly reproduced without the accompanying illustration.

Constitution of the Rhodinol of Essence of Pelargonium.—Ph. Barbier and L. Bouveault.—The principal portion of the essence of pelargonium is a colourless liquid, rather oily, having a very strong smell of roses, boiling at 115°—116° under a pressure of 10 m.m. At 0° its specific gravity is 0·8866, and it gives, in a thickness of 20 c.m., a deviation of −12° 28′. This compound is an alcohol, as is found by its ready transformation into acetic ether. Its composition is $C_{10}H_{18}O$. It is a cyclical compound and contains an atom of unsymmetric carbon.

Action of Thionyl Chloride (Chlorosulphurous Acid) on certain Mineral and Organic Compounds.—Ch. Mouren.—The author studies the action of thionyl chloride on the mineral acids, on oxalic and formic acids, and on the aldoximes. It yields with the mineral acids the corresponding chlorhydrines (monochlorhydrine and pyrodichlorhydrine) with sulphuric acid, and with the aldoximes the immediate products of dehydration or nitriles. Oxalic acid is decomposed with formation of carbon dioxide and monoxide, and formic acid with that of carbon monoxide.

Stability of Aqueous Solutions of Mercuric Chloride.—E. Barcker.—Dilute solutions of mercuric chloride prepared with ordinary water, with the addition of a slight proportion of hydrochloric acid, undergo merely insignificant changes on exposure to air and light, and are unalterable if withdrawn from this double influence. Solutions of mercuric chloride at 1/1000, mixed with ½ grm. tartaric acid per litre, are as permanent as those to which hydrochloric acid has been added.

Oxidation of Beer-Worts.—P. Petit.—The oxidation of the principles of the wort is very feeble at a low temperature, and is rendered active on ebullition. Wort at 60° gives per litre 2 c.c. of dissolved gases, of which only 0·11 c.c. are CO_2, and after saturation with air 16·5 c.c. of gas, 2·1 c.c. of which are CO_2. But after ebullition and saturation with air it yields 20·1 c.c. of gas, of which 3·8 c.c. are CO_2.

Can the Use of the Auer Gas-burner occasion Partial Poisoning?—M. Gréhaut.—The author has made experiments which in some quarters would be hotly denounced. He finds that the use of the Auer burner cannot occasion poisoning.

No. 6, August 6, 1894.

Spelæology.—French *savants* have invented this new term for the observations, geological and palæontological, made on the exploration of caverns.

Basic Calcium Salts.—M. Tassilly.—Lime has the property of combining with the haloid compounds of calcium to form basic salts. One of these, the oxychloride, $CaCl_23CaO16H_2O$, has been studied by Ditte. The oxybromide and oxyiodide form the subject of the present paper. Both these salts are in composition

analogous to the oxychloride, and both are decomposed by water, alcohol, carbonic acid, and the more energetic acids. They dissolve easily in the hydracids and in very dilute nitric acid. If this acid is not sufficiently dilute it decomposes the oxyiodide, liberating the iodine. Sulphuric acid converts these substances into sulphates. The solution heat of the oxychloride is 63·4 cals., that of the oxybromide 63·55, and that of the oxyiodide 63·3. The formation heats, proceeding from liquid water, are respectively 92·00, 98·85, and 103·30 cals. The compounds of the form $CaM_2,3CaO,16H_2O$, in which M represents the halogen, have approximately the same solution heat as the corresponding hydracids.

On the Use of Selected Ferments.—Charles Fabre.—From the author's experiments it results that ferments intended to produce fine wines cannot be sown in any must. Such ferments should be sown in a must of grapes derived from, or acclimatised for a long time in, the region whence the selected culture has been obtained.

MISCELLANEOUS.

University of Halle.—According to the *Chemiker Zeitung*, the honorary degree of M.D. has been conferred by the University of Halle upon Prof. Dr. Ostwald, of Leipzig; Prof. Dr. Pfeffer, of Leipzig; and Prof. Dr. Soxhlet, of Munich. Prof. Dr. von Helmholtz has received the honorary degree of Doctor of Laws from the University of Halle.

Chemical Manufacturers and their Critics.—A Mr. Aked, preaching at the "City Temple," delivered himself of the following outburst:—"Yet our laws permit the chemical labourers of St. Helens, in Lancashire, to be worked an average of twelve hours a day, year in and year out, to be scarred and burnt by flying particles of caustic, their teeth destroyed by acids, their internal organs to be blackened by vapours." It is to be feared that the Reverend orator has obtained his facts, not from personal observation or from the accurate accounts furnished by Dr. J. T. Arlidge and Dr. Watson Smith, but from the exaggerated and sensational statements which appeared last year in a certain morning paper. If it had suited his purpose to ascertain the truth, he would find the twelve hours a day, "year in and year out," shrink to thirty-four hours weekly at the least agreeable work under the Alkali Union, and thirty-six hours weekly at the Widnes Alkali Works. (See Chemical News, vol. lxvii., p. 179).

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SESSION 1894—95.

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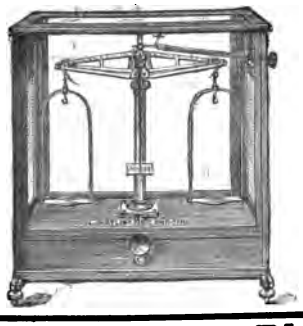

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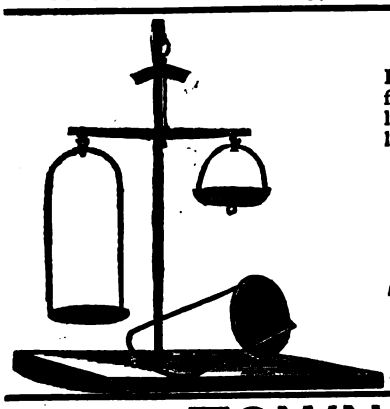

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THE CHEMICAL NEWS.

Vol. LXX., No. 1815.

POPULAR METHOD FOR ESTIMATING CARBON DIOXIDE IN AIR.*

By J. B. COHEN, Ph.D., and G. APPLEYARD, Yorkshire College.

The method depends upon the fact that if dilute lime-water, coloured with phenolphthalein, containing insufficient lime to combine with the carbon dioxide present, is shaken with the sample of air, the rate of absorption of the gas will vary with its volume. The time required to decolourise the indicator will therefore give the quantity of dioxide present.

The following apparatus and chemicals are required:—

1. A clear glass stoppered bottle of 22 ozs. capacity.
2. A solution of phenolphthalein prepared by dissolving 0·2 grm. in 100 c.c. of equal volumes of alcohol and water.
3. A standard lime solution prepared by diluting 10 c.c. of saturated lime-water to 1 litre.
4. Hand-bellows for aspirating the sample of air.

The process is conducted as follows:—

The bottle is rinsed out with water and drained for a minute, and the sample of air is then aspirated by means of the bellows.

One-third c.c. of indicator solution and 10 c.c. of dilute lime-water are added, and the bottle stoppered and well shaken with both hands until the pink colour vanishes. The time required will indicate the condition of the atmosphere.

The following determinations have been made in which the amount of carbon dioxide has been ascertained by Pettenkofer's method:—

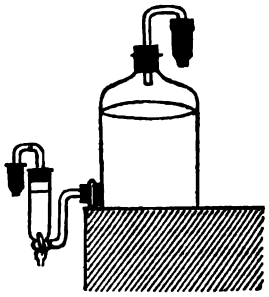
Time in mins. required to decolourise the solution.	Percentage of CO_2 by Pettenkofer's method.
1¼	0·16
1¾	0·138
1½	0·128
3¼	0·077
3½	0·070
4	0·053
4½	0·051
5	0·046
5¼	0·044
6¼	0·042
7½	0 035

The following table may be taken to indicate roughly the condition of the air:—

Time.	Condition of the air.
Under 3 minutes.	Bad.
Above 3 and under 5 mins.	Fair.
Above 5 mins.	Good.

In place of a separate measuring vessel for the lime-water, a pipette-tap of the form shown in the figure may be attached to the stock bottle of lime-water. It consists of a three-way tap fused on to a tube graduated for 10 c.c. The opposite limb of the tap is drawn out into a nozzle, whilst the third limb is bent twice at right angles and is inserted into the tubulus of the stock-bottle. To the open end of the pipette a small soda-lime tube is attached. By turning the tap horizontally the liquid flows into the pipette. When it reaches the mark the tap is turned through 45° and thereby closed. The liquid is run into the testing bottle by turning the tap vertically.

The apparatus may be simplified and made more portable by using sealed glass tubes containing 10 c.c. of the standard lime-water coloured with phenolphthalein.



These tubes are broken in the testing bottle, and the bottle shaken until the colour vanishes.

At our request Messrs. Reynolds and Branson, of Leeds, have kindly undertaken to supply the necessary apparatus and reagents at very little above cost price.

* A Paper read before the British Association, Oxford Meeting Section B.

SOME EXPERIMENTS WITH FREE HYDROXYLAMINE.*

By Dr. LOBRY DE BRUYN (Amsterdam).

In a few words I may remind you that the preparation of the free base can be performed in the following way. The hydrochlorate of the base is dissolved in absolute methyl alcohol, the equivalent quantity of methylate of sodium is added, the common salt which precipitates in filtrated off, and the solution of the free base concentrated by distillation at 100 or 200 m.m. By fractionating the residue at the pressure of 20 m.m. the pure free base passes over at 58° as a crystallised substance melting at 33°, of a high specific gravity (1·35), without odour and volatile.

The reason why the free hydroxylamine must be distillated at a low pressure is that the substance is a rather violently explosive one, and that explosion occurs spontaneously at the temperature of about 130°. Thus care must be taken never to heat the substance too strongly, for if heated at the ordinary pressure to 70° or 80° an explosion may occur, the self-decomposition raising the temperature. The hydroxylamine is an endothermous compound and can be transformed totally into gaseous products, the two conditions which, as is known, characterise an explosive. I have produced the explosion in the following manner:—1 or 1½ c.c. of the melted base were put into an ordinary open test-tube with a thermometer in it, the tube stood in an ordinary beaker which acted as an air-bath heated by a burner. When the temperature had reached 90° the flame was withdrawn; the self-decomposition was already vigorous, the temperature rose spontaneously to 130°. Then a violent explosion took place, the glass apparatus was reduced to powder, the copper gauze on which the vessel stood was torn to pieces, phenomena which prove that the explosion is of the same nature as that of the high explosives. If one drop of the melted base in a tube is brought in a flame you hear a loud explosion.

The free base can burn in the air with a yellowish flame.

That hydroxylamine is a highly reducing agent is known already, since Lossen, about thirty years ago, dis-

* A Paper read before the British Association (Section B), Oxford Meeting, 1894.

covered the salts of the base. It is obvious that the free base must show the reducing properties in a much higher degree. Already on exposure to the air at the ordinary temperature it gradually attracts oxygen; one of the products of the oxidation is, as you see, nitrous acid. When the free surface in contact with the air is great, the oxidation can be accompanied by a rise of temperature; so, for instance, if some filter paper or asbestos is moistened with the melted substance. A current of oxygen passing over the substance provokes the formation of fumes containing nitrous acid, the temperature rising at the same time.

It is not surprising that oxidising agents act violently with the free base; so, for instance, the solid permanganate of potassium, chromic acid, and some peroxides, in contact with some drops of the substance, produce an inflammation. Powdered bichromate of potassium provokes a sharp detonation; solid iodate of sodium and nitrate of silver are also reduced instantaneously. The action of anhydrous sulphate of copper is also very violent, the reduction of the salt can be accompanied by inflammation.

Metallic sodium also acts violently, producing a flame. If the action is moderated by adding some dry ether hydrogen is evolved and a white substance, $NaONH_2$, is formed. This compound is a dangerous one, because it explodes in contact with the air.

The halogens act vehemently with the free base; chlorine inflames the substance; bromine and iodine disappear immediately, producing the corresponding acids, water, and nitrous oxide.

As to the solvent properties of the free base, these are nearly equal to those of water. It dissolves different salts; some of them, as for instance KI, in great quantity. Gaseous ammonia introduced at 16° in the melted base is dissolved rapidly and gives a solution containing 20 per cent of the gas.

In the same way the substance behaves like water with respect to other liquors; it is consequently only easily soluble in the alcohols, and nearly insoluble in the ordinary organic liquors. Methyl and ethyl alcohol are miscible with the melted base in every proportion; these solutions, however, below the melting point of the base are supersaturated with respect to the solid compound. There exists, however, a difference between fluid hydroxylamine and water, the former not being miscible in all proportions with propyl alcohol.

That hydroxylamine can occupy the place of the hydrate water in salts has been proved by Crismer, who has prepared the salts $ZnCl_2 2NH_2.OH$, $BaCl_2 2NH_2.OH$, &c.; by means of dry ammonia Crismer has prepared the free base from these double compounds.

The presence of the hydroxyle group in hydroxylamine explains the analogies between this substance and water; the difference in their behaviour must be explained, at least partly, by the greater molecular weight of the former compound.

Solid caustic soda is also very soluble in the melted base; care must be taken to cool when adding the soda. This solution is much more liable to oxidation than the free base; exposed to the air the solution can spontaneously inflame. So we see that the presence of alkali (or rather of $NaONH_2$) increases in a high degree the liability to oxidation, the free base oxidising not so quickly as the solution of NaOH in it, while the solid $NaONH_2$ explodes in contact with the air.

Although, as has been shown, free hydroxylamine is a strong reducing agent it can be reduced itself by means of zinc dust. If this substance is moistened with the base (in an atmosphere of nitrogen) a pretty violent reaction occurs five or ten minutes later, ammonia and zinc oxide being formed.

More particulars concerning free hydroxylamine were published some years ago in the *Recueil des Travaux chimiques des Pays-Bas.*

NOTES ON WATER ANALYSIS.

By C. A. SEYLER, B.Sc.

(Continued from p. 105).

II. *Carbonic Acid (continued).*

In order to test the method of estimating free carbonic acid it is necessary to have a standard solution of carbonic acid, or some independent method of control. In view of the uncertainties attending Pettenkofer's method, I preferred the former alternative. N/20 solutions of sodic carbonate and hydrochloric acid were prepared so as to correspond exactly, with methyl orange as indicator. The standard solution of carbonic acid was prepared by mixing equal volumes of these solutions in presence of enough distilled water to make the volume about 100 c.c. By running in the acid cautiously from a burette with a long spit, and gently mixing the contents, it is possible to avoid loss of CO_2. This solution was immediately titrated with sodic carbonate under the usual conditions. An allowance has to be made for the free CO_2 in the distilled water, which was separately titrated.

1. 5 c.c of each solution mixed required 5·7−0·57=5·13
2. „ „ „ 5·4−0·5 =4·9

In other experiments the water was first neutralised to phenolphthalein, and then the solutions added.

3. 10 c.c. of each, mixed, required 10·2 c.c.
4. „ „ „ 10·1 „

This shows that free CO_2 can be titrated in this way with sufficient accuracy. That this is also true in presence of sodic bicarbonate is shown by the following results. Neutral solutions of bicarbonate were prepared by mixing the above solutions. From a bicarbonate, a mineral acid will liberate two equivalents of carbonic acid.

1. 5 c.c. N/20 bicarbonate add 2·5 acid, required 5·0 alkali
2. „ „ „ „ 4·9 „

Pettenkofer's method is the one that has hitherto been almost exclusively used for the estimation of carbonic acid. For the purposes of the busy analyst it is too complicated, involves the use of many glass vessels, frequent measurements of large quantities by the pipette, and repeated standardising of solutions. The results when obtained give the volatile CO_2, a quantity made up of two distinct parts, the half-bound and free, which deprives it of its chief hygienic import. Moreover, the results are subject to considerable uncertainty, especially in the presence of magnesia, and even under the most favourable circumstances Tiemann ("Chem. Analyse des Wassers") admits that duplicates may vary from 0·5 to 1·0 m.grm. of CO_2 per 100 c.c. Trillich's proposed modification, involving a gravimetric estimation of magnesia, is still less practicable. The method is thus unfit for estimating free carbonic acid by subtracting a quantity equal to the combined CO_2, representing the half-bound acid. The experimental errors are then comparable with the quantities to be estimated. On the other hand, two simple titrations will give us the free and combined CO_2 directly, and their sum is the quantity sought in Pettenkofer's method. Although the difficulties of the older method have not been overcome, I thought it necessary to make a few comparisons of the two methods, and in this I must acknowledge the help of Mr. F. Harris, who has independently checked some of my results. N/20 solutions were used, and phenolphthalein the indicator when ammonium salts were absent. In the possible presence of magnesia, ammonic and calcic chloride were added, and rosolic acid used as indicator—adding the same amount of ammonic and calcic chloride in standardising the lime-water to eliminate any disturbing influence.

(Results stated in c.c. N/20 per 100 c.c. water; to get m.grms. multiply by 1·1).

Free CO_2 *Alone.*

Trillich.	Pettenkofer.
6·7	6·9, 7·6
13·7	14·2, 14·5

Half-bound CO_2 *Alone.*—Solutions of $CaCO_3$ in carbonic acid were agitated until just a faint pink to phenolphthalein on filtering, and the combined CO_2 estimated by acid and methyl orange.

Combined.	Free.	Sum.	Pettenkofer.
9·5	nil	9·5	10·7
7·3	nil	7·3	8·5

Contrary to expectation, Pettenkofer's method gave persistently higher results, and this was also the case when both free and half-bound CO_2 were present (as calcic bicarbonate).

4·3	0·2	4·5	5·05
4·3	8·0	12·3	13·3, 13·9
1·0	7·0	8·0	8·9
14·6	5·6	20·2	22·1

With magnesic bicarbonate, the differences were somewhat greater.

4·5	0·2	4·7	6·8
4·1	0·2	4·3	5·7

Whether these results represent real differences remains still to be determined.

With natural waters the differences were almost as constantly in the other direction and of about the same magnitude, except in the third experiment, where it is unusually large.

3·6	0·5	4·1	4·3
2·3	3·3	5·6	4·1
4·8	5·5	10·3	8·4
8·8	5·0	13·8	13·1
8·7	4·7	13·4	13·5, 12·9
11·1	4·0	15·1	14·1

Considering the uncertainties of Pettenkofer's method, I think the above results confirm what I may call the Lunge-Trillich method, and justify the assumption that the half-bound CO_2 may be put equal to the combined when the reaction is neutral or acid to phenolphthalein.

It now remains to speak of the practical results of the systematic use of the method. Experiment shows that the free CO_2 is more easily lost than the half-bound, thus justifying the name. Even very strong solutions of calcic bicarbonate, containing much free CO_2, will have the greater part of the latter removed by a current of air, the combined CO_2 being only slightly reduced, in one case from 49·8 to 48·4 m.grms., and in another from 27·5 to 26·4 m.grms. More precise are the following experiments, in which the solutions were exposed in beakers.

$CaCO_3$—		After 18 hours.	After 3 days.
Free CO_2	4·9	2·2	0·33
Combined CO_2 ..	4·8	4·8	4·8
$MgCO_3$—			
Free CO_2	4·4	1·8	0·33
Combined CO_2 ..	4·6	4·6	4·6 *

It is thus to be expected that surface waters will be characterised by a very low free CO_2, and this is in general the case. The value of any chemical estimation depends on the extent to which it characterises the water and throws light on its previous history. This low free CO_2 is highly characteristic of all pure surface waters.

Rain-water is the ultimate source of all supplies, and as it never comes into contact with much carbonic acid, it may be expected to be deficient in both kinds. I have only once examined a sample of recently-fallen rain-water, taken in the neighbourhood of Swansea, and found free CO_2 0·44 m.grm., and combined CO_2 0·04 per 100 c.c. (by method of Mylius and Foerster).

Upland surface water differs little from rain water in respect to contact with carbonic acid. Of this there are many examples in Wales, and the Swansea supply is typical. The free and combined CO_2 are about equal, and rarely reach as much as 0·5 m.grm. per 100 c.c. As a rule, the free CO_2 is about 0·2 to 0·3, and the combined 0·3 to 0·4 m.grm. The water from the river Rhondda is of a similar nature, containing constantly free CO_2 0·2, combined CO_2 0·2 m.grm. The supply from catch-water reservoirs at Carmarthen gave free CO_2 from 0·2 to 0·5 m.grm., and combined 1·9 to 2·1.

Of *mixed surface waters*, originally derived from springs and surface-water, I have not much experience, but the example of the Thames shows that we may expect the free CO_2 to be as low as in the upland surface, while the combined CO_2 may be considerable (in the case of the Thames 7 to 9 m.grms.). In brook water I have found free CO_2 from 0·2 to 0·4, and combined from 1·0 to about 7·0 m.grms.

In surface waters living organisms, animal and vegetable, may play an important part in regard to the carbonic acid. When a water is so loaded with organic matter that active fermentative changes take place, a large amount of carbonic acid may be produced, as exemplified by Miller's well-known experiments on the Thames. The following are examples of a highly impure pond water:—

	Free CO_2.	Combined CO_2.	Free O. C.c. per litre.
A	3·1	10·3	0·14
B	1·5	8·0	4·03

Sewage and effluents may therefore be expected to contain much carbonic acid, both combined and free. The following are cases in point.

	Free CO_2.	Combined CO_2.	Cl.
A. Culvert of main sewer	3·2	16·9	7·0
B. Bed of river opposite culvert	6·6	23·1	7·0
C. From culvert	2·75	33·5	9·8
D. From stream near culvert ..	13·7	21·5	8·5
E. Sewerage (effluent)	2·6	11·0	2·5
F. Stream above entrance of E..	0·88	5·8	0·9
G. Stream below „ „ ..	1·3	6·2	1·0

In none of the above was any free oxygen present, and the combined CO_2 was largely present as ammonic bicarbonate, especially in B; in which, also, butyrates were found in notable quantity. The carbonic acid is, in these cases, chiefly the product of bacterial activity. On the other hand, green plants rapidly remove carbonic acid. While exposure to air removes chiefly the free CO_2, plants can take their carbonic acid both in the free and half-bound states, and must thus tend to precipitate the dissolved carbonates. This is proved by experiments upon sea-water, a case of surface water of peculiar interest.

Application of the above methods showed the curious fact that sea-water, if pure, is normally slightly alkaline to phenolphthalein*, and therefore can contain no free carbonic acid. This confirms the results obtained by other methods (see Thorpe's "Dict. Applied Chem."). Pure sea-water from the Gower coast was repeatedly tested with the following results:—

100 c.c. required to destroy the pink 0·35 c.c. N/20 acid. Total alkalinity with methyl orange 4·7 c.c. N/20 acid. This gives the carbonic acid.

* Compare Bernard Fischer and Piefke (*Zeit. Hyg.*, xiii.).

* I can only speak for the water near the coast here at Swansea.

		M.grms.
Free CO_2		none
Combined CO_2 ..	$4·7 \times 1·1$	$= 5·17$ per 100 c.c.
Half-bound CO_2 .	$(4·7 - 0·35 \times 2) \times 1·1 = 4·4$	,, ,,
Total CO_2		9·57 ,, ,,

That green plants can take their carbonic acid from bicarbonate follows from the fact that they immediately liberate oxygen from sea-water when exposed to sunlight. Two experiments were made, one with normal, slightly alkaline sea-water; and the other, with sea-water rendered strongly acid to phenolphthalein by CO_2, both being exposed to the action of green Ulva in sunlight. Check experiments without the green plant were made simultaneously. The plants liberated oxygen in both cases, and rendered the water very strongly alkaline to phenolphthalein.

Ordinary Sea-water.

	Blank.	After action of Ulva.
Free CO_2	none	none
Half-bound	4·5	0·99
Combined	5·4	4·7

Sea-water with Free CO_2 Added.

Free CO_2 ..	4·7	9·1	none
Halfbound ..	4·4		2·6
Combined		4·4	6·1

(The increase of combined CO_2 in the last case is no doubt due to the solvent action of the free CO_2 upon the coralline sea-weed present).

It is interesting to note that the process appears to stop before all the half-bound CO_2 is removed. This seems to occur when a definite amount of monocarbonic CO_2 is present; in the above cases the amount is 3·71 and 3·5 m.grms. respectively. In two further experiments 3·44 and 3·42 m.grms. were found after the action had apparently ceased.

(To be continued.)

NEW RESEARCHES ON THE INFRA-RED REGION OF THE SOLAR SPECTRUM.

By Prof. LANGLEY.

In September, 1882, I submitted to the Academy a communication entitled "Observations on the Solar Spectrum," accompanied by a figure of the curve of energy of the infra-red spectrum obtained by means of a glass prism. On referring to this curve we see that below the wave-length 1·2 μ we have obtained only twelve inflections, great and small, including the great band, the wave-length of which is about 1·8 μ, the band which I have since designated as Ω, the existence of which has been established with precision by the observations made at Mount Whitney. It will be remembered that the existence of heat has also been established at a distance of nearly 3 μ, the limit at which the prism ceased to transmit the radiation.

Photography has not succeeded in representing a much larger part of the infra-red than the eye has been able to perceive, considering that the rays whose wave-length exceeds 0·8 μ can be distinguished with the naked eye, and I do not know that photographs have been published giving radiations the length of which is much above 1 μ.

Certain interesting results have been obtained even below this point (1 μ) by procedures of phosphorescence. But, if I am not mistaken, the curve given in my communication to the Academy comprised our principal actual knowledge concerning the extreme region, around and beyond Ω in the spectrum of a glass prism. These inflections were obtained and determined by means of the bolometer, and by a procedure so slow as to leave us no prospect of carrying our measurements much further.

In 1890 the Congress at Washington authorised certain astrophysical researches, the execution of which was intrusted to the Smithsonian Institute. Thanks to the experiments conducted in the last years, we have at last succeeded in substituting for the slow and personal method just referred to, another, which—though founded on the use of the bolometer—is almost automatic, and which, whilst much superior to the old method in precision, is at the same time incomparably more rapid and delicate.

The bolometer and its appendages have been improved in such a manner that they are not confined to indicating a change of temperature; they also give its value where its variations are below one-millionth of a degree C., since they are shown in the metallic ribbon of the bolometer, which has $\frac{1}{20}$th m.m. in diameter and $\frac{1}{200}$th m.m. in thickness.

Clockwork of great precision moves the spectrum in such a manner that each of the rays, visible or invisible, passes successively over the ribbon, which meantime, on account of its slight mass, changes its thermic equilibrium in so short a time that it may be regarded as insensible. Since what is dark to the eye is cold to the bolometer, the presence of an invisible absorption ray is indicated by an almost instantaneous deflection of the galvanometer.

This deflection was formerly shown to the eye upon a scale. At present there is substituted for the scale a sensitive photographic plate, moved in a vertical direction by the same perfect wheelwork which passes the spectrum over the bolometer. It follows that the curve of energy is registered in a perfectly automatic manner by means of photography, with the aid of the bolometer, in regions hitherto quite inaccessible to photography alone.

A perfect synchronism being thus secured in the movement of the photographic plate and of the distant circle which carries the prism, we see without difficulty that the curve traced automatically can show us at first sight not merely the magnitude of the variations of the temperature of the spectrum, but also the exact part of the spectrum where they are produced.

Not many dozens, but thousands, of deflections, corresponding to the Frauenhofer rays of the visible spectrum, may thus be registered; and we can now obtain with precision, in an hour, results which could not be obtained with the micrometer, even at the cost of many years of arduous work, so well that we may take for comparison in one and the same day several representations of the entire spectrum. These, as well as others obtained on different days, are submitted to a strict comparison by a method which checks the existence of each inflection, at the same point of all the curves thus traced independently of each other, with a probable error of position which corresponds to less than a second of an arc. On thus examining the lower invisible spectrum, we discover that it is the seat of absorption, at least as complex as those produced in the visible spectrum, and the new method already distinguishes more than 2000 invisible rays. The maps of this region, hitherto unknown, will soon be published.

To prove to what extent the new method possesses the power of separation, we may apply it not only to the invisible spectrum, where for the present our word must be taken for the results obtained, but to the visible spectrum, where it may be applied to the study of a known region, *e.g.*, that of the ray D. Our apparatus, purely thermometric, not merely resolves this ray into its two elements, but reveals the ray of nickel found in the middle. This is the well-known test of visual spectroscopes of considerable power.

The graphic trace, on the contrary, is automatic, and of a double effect. We have, firstly, the curve of energy obtained automatically; the abrupt inflections are due to the extreme sensitiveness of the apparatus. It regis-

ters photographically the variation of temperature produced by each of the rays, which separately are invisible unless magnified.

A method the details of which will be given in a future communication renders it possible to convert this curve of energy into a linear spectrum. This linear spectrum, which the author gives in his memoir, is obtained by an automatic procedure applicable to all parts of the spectrum. Although the known angular distance between the rays D, in the spectrum given by rock-salt, scarcely exceeds 10 seconds of the arc, the ray of nickel appears so separate from its neighbours that the possibility of a much further resolution appears evident. The instrument can separate rays whose interval does not exceed 2 seconds. Now, since this purely thermometric process is applicable in the total extent of the invisible heat spectrum given by a prism of rock-salt on a surface of 2° (say 7200″), we may say that this procedure has a power of resolution capable of revealing to us thousands of rays if they exist.

Taking the instance of these D rays, my object has been to inspire confidence in the assertion that the entire inferior infra-red spectrum, from 1·2 μ to 6 μ, may now be reproduced automatically by a process giving hundreds of rays for each ray known hitherto, and that the relative position of each will be given with a precision hitherto unknown for measurements of this kind.

Let us add that not merely the greater part of the solar energy is found in this little-known region, but the absorptions seem to be due to our atmosphere rather than to that of the sun. Hence it is not improbable that their study may supply a precious means for foreseeing the variations which influence meteorological perturbations.—*Comptes Rendus*, cxix., p. 388.

EXPERIMENTS IN THE LIQUEFACTION OF HYDROGEN.*

The strenuous efforts now being made by physicists to approach the zero of temperature are in some ways analogous to the numerous attempts that have been made, or are now being made, to reach the North Pole. It must be confessed, however, that the geographical quest has the enormous practical advantage of appealing forcibly to the popular imagination, while the interest and importance of the physical inquiry are appreciated by a comparatively small section of the community. In both cases success may be said to depend upon equipment, persistency, and the selection of the right road. In neither case can the anticipated results be considered as likely to be of immediate practical value. The North Pole will not be the signal-post of a trade route, and the condensers of our engines are never likely to reach the zero of temperature. If the latter could be obtained, however, the results would be highly practical, because we should then completely transform heat into mechanical power, instead of getting only 10 per cent converted by our present means of working.

The solution of the problem of the North Pole will add greatly to our knowledge of physiography, and the approach to the zero of temperature will open out fields of investigation where matter and energy can be examined under new conditions. The parallel between getting to the Pole and reaching the zero of temperature breaks down, however, when examined a little more carefully. There seems to be no reason why man should not attain the 90th parallel of latitude as well as the 75th; but in the case of temperature there are strong grounds for the belief that the zero can never be reached. The temperature of celestial space can only be approached in the laboratory, yet the nearer we get to it the more important physical problems become.

Up to the present liquid air or nitrogen is the agent that has been most successfully used in such investigations. When liquid nitrogen is evaporated *in vacuo*, a temperature of about 210° C. below the melting-point of ice can be just reached, but the practical working limit in such experiments is about *minus* 200° C. This temperature is still 74° from the zero, and the question now is, Can we diminish the distance? The zero may be defined as that point of temperature at which gas particles would give no pressure and have no volume. The temperature at which this would take place is 274° below the freezing-point of water, and this result is confirmed by thermodynamical considerations where temperature is defined apart from the properties of any particular kind of matter. The only avenue of approach that is left seems to be the liquefaction of hydrogen, which is the sole remaining gas that has not been liquefied. It is true all the text-books state the reverse, on the ground that it has been proved that compressed hydrogen when expanded can yield a mist. Such statements have added nothing to the advance of knowledge in this department. On the contrary, they have done harm by making the ignorant believe that the most permanently gaseous element has been vanquished. The attainment of any such result is, indeed, a problem surrounded by almost insurmountable difficulties.

The possibility of making a gas pass into the liquid state depends upon our being able to get below the point of temperature known as the critical point. Unless this point is reached no amount of pressure can force the gas into the liquid condition. Now, hydrogen has a critical point of about minus 240°, and the question is, How can we attain such a temperature, seeing that liquid air or nitrogen only enables a temperature of minus 200° to be reached? How can these 40° or 50°, as the case may be, be bridged over? This can only be done by constructing a new substance, having a critical point of minus 200°, or some 50° lower than nitrogen, which is the most volatile known liquid. Such a body can be made by liquefying a gas composed of hydrogen mixed with 10 per cent of nitrogen. This is the direction in which Prof. Dewar has been lately pressing forward his investigations, and the new results give hopes of further advance. The really serious question is the extremely small proportion of the liquefied material that can be collected in open vessels. In order to understand this it is necessary to keep in mind that, when a substance is near its critical point, it has a very small latent heat of evaporation, but a very high specific heat. It follows therefore that, in order to get the liquid cooled by its own evaporation from near its critical temperature to its boiling-point, a very large proportion of the liquid produced under high compression in the refrigerating apparatus has to be sacrificed. Thus, for instance, one pint of liquid air collected in one of the well-known open vacuum vessels necessitates the liquefaction of some three pints of liquid in the apparatus In other words, two-thirds of the original amount of liquid produced has to evaporate in order to procure the remaining third at its own boiling-point. The proportion of the resulting liquid in each case depends, as above stated, on the latent heat of evaporation and the specific heat of the particular liquid,—if we neglect for the present the serious question of cooling the vessels,—and the loss of heat by radiation and conduction. All our present experience confirms the view that the latent heat of evaporation is proportional to the absolute critical temperatures, or, what is about the same, to the absolute boiling-points. As the absolute critical point of hydrogen is about 40°, while that of nitrogen is 128°, it is clear that the latent heat of liquid hydrogen would only be one-third that of liquid nitrogen or air. Further, analogy leads us to the conclusion that the specific heat of liquid hydrogen is very much greater than that of liquid nitrogen or air. The combined result must therefore be that, if practically

* *The Times*, September 1st 1894.

only 30 per cent, as above described, of liquid nitrogen or air can be collected, a very much smaller amount of hydrogen, say from 1 to 5 per cent, is all we can anticipate as the yield by similar methods of manipulation. Assuming that we had such a liquid, its use as a cooling agent would indeed be very expensive, since its cost may be taken as at least twenty times the cost of liquid air. One thing, however, can be proved by the use of the gaseous mixture of hydrogen and nitrogen, viz., that by subjecting it to high compression at a temperature of *minus* 200°, and expanding the resulting liquid into air, a much lower temperature than anything that has been recorded up to the present time can be reached. This is proved by the fact that such a mixed gas gives, under these conditions, a paste or jelly of solid nitrogen, evidently giving off hydrogen, because the gas coming off burns fiercely. Even when hydrogen containing only some 2 to 5 per cent of air is similarly treated, the result is a white solid material (solid air) along with a clear liquid of low density which is so exceedingly volatile that no known device for collecting it has been successful. To attain such a result it is necessary to liquefy and expand more than one pound weight (or about seven cubic yards) of hydrogen gas. Knowing the difficulties, from having to deal in the liquid state with the accumulated small impurities in such large amounts of gas, Prof. Dewar will not declare that he has had pure liquid hydrogen in one of his vacuum vessels, although what this liquid can be except hydrogen it is impossible to say.

The future progress of these costly and difficult experiments must depend very much upon questions of outlay, and it is to be hoped that the public will not assume that the endowment so handsomely given to the Royal Institution by Mr. Ludwig Mond for the maintenance of a public laboratory of research, to be called the Davy-Faraday Laboratory, can be used for the prosecution of such investigations.

TWELFTH ANNUAL REPORT OF THE COMMITTEE ON INDEXING CHEMICAL LITERATURE.*

The Committee on Indexing Chemical Literature presents to the Chemical Section its Twelfth Annual Report. During the current year the following bibliographies have been printed in the channels indicated :—

1. "Index to the Literature of Didymium, 1842-1893." By A. C. Langmuir. *School of Mines Quarterly* [Columbia College, New York], vol. xv., pp. 33—47. November, 1893.

In this index the author follows the plan originally proposed by H. C. Bolton in 1870.

2. "The Tannins: a Monograph on the History, Preparation, Properties, Methods of Estimation, and Uses of the Vegetable Astringents." With an index to the literature of the subject. Vol. II. The Tannins of Oak-bark, Mangrove, Canaigre, Chestnut. By Henry Trimble. Philadelphia. 1894. Pp. 172. 12mo. Ill.

This forms the second volume of the work previously noted in our reports. The carefully compiled bibliography contains about 325 titles.

Reports of progress have been received from several chemists :—

Prof. Arthur M. Comey announces that the first volume of his "Dictionary of Chemical Solubilities," devoted to inorganic compounds, has gone to press, and will be published before the close of the year. The second volume is also in active preparation.

Dr. Alfred Tuckerman reports that the United States section of his "Bibliography of Mineral Waters" will be ready for the printer in a few months.

Prof. Clement W. Andrews states that he had done much work on a "Bibliography of the Polariscopic Determination of Sugar"; but learning that Prof. H. W. Wiley, chief chemist of the U.S. Department of Agriculture, was engaged in a similar undertaking, generously handed over to him all the material he had accumulated. The combined manuscripts have recently been returned to Professor Andrews, who will continue the work.

Prof. H. W. Wiley reports great activity on the part of the Division of Chemistry of the U.S. Department of Agriculture in the preparation of bibliographies and special indexes, but he is obliged to admit difficulties in securing the printing of the manuscripts. We quote the following paragraphs from his letter dated June 29, 1894, addressed to the chairman of the Committee :—"The elegant bibliography of heavy metals occurring in canned goods, by Mrs. K. P. McElroy, has not yet found an avenue for publication." . . . "We also have a very complete bibliography of carbohydrates from the point at which they were left by Tollens in his "Handbuch," in 1888, up to the close of 1892. This work was partly done by myself, but chiefly by Mr. H. E. L. Horton, and we were assisted greatly by receiving many hundred titles from Prof. C. W. Andrews of the Massachusetts Institute of Technology. But what we can do with such a bibliography, comprising as it does three or four thousand titles, I do not know. The Department of Agriculture will not publish it, it is too large for the *Journal of the American Chemical Society*, and so it lies idle." . . . "A very complete bibliography of agricultural chemistry for the year ending 1893 has also been completed by the committee appointed by the Association of Official Agricultural Chemists, of which Dr. William Frear is chairman. This bibliography I submitted to the Assistant Secretary of Agriculture with the request that it be published as a part of the *Proceedings* of the Association, but this request was not complied with. The same Committee has in preparation a complete bibliography of agricultural chemistry for the year ending June 30, 1894, and this report will be presented to the meeting of the Association of Official Agricultural Chemists, in August, at Washington. We shall then have unpublished a complete bibliography of all agricultural chemical topics for the two years ending June 30, 1894."

Mr. P. H. Seymour's "Bibliography of Aceto-acetic Ester" is in the printer's hands, and will be published by the Smithsonian Institution during the summer.

Prof. F. W. Clarke reports that he is engaged on a new edition of his "Re-calculation of Atomic Weights."

Prof. H. C. Bolton has begun a Supplement to his "Bibliography of Chemistry," and last winter visited the chief libraries of Italy in search of material.

Dr. H. P. Talbot, of the Massachusetts Institute of Technology, with the co-operation of Dr. H. C. Bolton, has begun a second edition of the "Index to the Literature of Manganese" published by the latter in 1875, with the intention of bringing it down to date.

Prof. James Louis Howe, of Louisville, Ky., reports progress on a "Bibliography of the Platinum Metals."

Dr. W. H. Magee, of Cornell University, has completed Indexes to the Literature of Cerium and of Lanthanum, and the MSS. have been approved by your Committee, and, together with Mr. Langmuir's "Index to the Literature of Didymium," have been recommended to the Smithsonian Institution for publication. The three indexes have been accepted by the Smithsonian and will appear in the Miscellaneous Collections.

Prof. Charles E. Munroe reports that Part II. of his "Index to the Literature of Explosives" does not complete his work, as stated in the Eleventh Annual Report; he is engaged on a continuation.

Dr. Claude Augustus Oscar Rosell's thesis presented to the Columbian University, Washington, D.C., in June, entitled "Investigation of the Properties of Ferric Acid,"

* Advance proofs from vol. xliii., *Proceedings of the American Association for the Advancement o Science.*

contains an exhaustive bibliography of the ferrates and ferric acid; the channel of publication is not yet determined.

Prof. J. Christian Bay reports progress on a "Bibliography of Alcoholic Fermentation," and has commenced a "Bibliography of Glycogen."

The annual reports of this Committee are properly confined to the productions of Americans, but the Chairman begs leave to direct attention to indications of a growing appreciation of the value of special bibliographies on the part of European chemists, confirming by their recent and proposed activities the work begun in America, at the Chairman's suggestion, now more than twelve years ago. Several European countries have long published periodical Bulletins of all books issued in their own lands, but they are as a rule too comprehensive in scope for the convenience of the specialist in science. Since the "Biblioteca Historico Naturalis," published at Göttingen, dropped chemistry from its pages (in 1887) the most useful bibliography of current scientific works has been the well-known "Naturæ Novitates" (Friedlaender, Berlin), now in its sixteenth year; however, this trade serial is stronger in German than in other languages, and falls short of the completeness desirable.

In technology and technical chemistry the admirable "Repertorium der technischen Literatur" (Leipzig), in its continuation, affords invaluable assistance to the industrial chemist. Recently, too, the following periodical has been established, *Biblioteca Polytechnica: Internationale Bibliographie der gesammten neuen Technischen Literatur, Herausgegeben von Fritz von Szczepanski*, St. Petersburg and Leipzig, 1893, 8vo., 12 numbers per annum. This includes chemistry pure and applied.

The need of an exhaustive authoritative bibliography of current chemical books of the world is still felt.

In a private letter to the Chairman of your Committee, Dr. Bechhold, of Frankfort-on-Main, announces his intention of publishing a full and complete "Index to Current Chemical Literature," in all languages, on a most comprehensive plan; the first number of this serial will be awaited by chemists with great interest.

Heinrich Wien (Vienna) and F. A. Brockhaus (Leipzig) announce the publication of a "Universal Index to the World's Technical and Scientific Literature." This ambitious undertaking is intended to embrace both books and periodicals and to represent all the known literature that has appeared in every part of the world; five parts are projected, viz., chemistry, medicine, mining, photography, electricity.

As most of the members of the Chemical Section are aware, a call has been issued for an International Congress of Applied Chemistry to be held under the patronage of the Belgian Government, at Brussels, in August, 1894. At that meeting it is proposed to found a *Review of Reviews of Applied Biological Chemistry* in several languages, to contain a résumé of chemical work in that branch from all parts of the world. The Secretary-General of the Congress is Monsieur Sachs, 68, Rue d'Allemagne, Brussels.

At the Congress of Chemists held in Chicago, in August, 1893, your Chairman had the honour to read an address on an "International Index to Chemical Literature" (*Journ. Am. Chem. Soc.*, xv., Oct., 1893), in which he proposed a simple scheme for indexing current periodical chemical publications by international co-operation. It is extremely gratifying to record that the necessity of international co-operation has since been suggested by so weighty an authority as the Royal Society (London). That splendid monument of the bibliography of science, "The Catalogue of Scientific Papers," published by the Royal Society, has failed to satisfy the requirements of students in science owing to the lack of a subject-index to the prodigious material classified under the names of the authors; but, according to a circular issued by the Royal Society in April, "it is hoped that a key-to the volumes already published may be eventually issued." The Royal Society further announces its intention of continuing the "Catalogue of Scientific Papers" after Jan. 1, 1900, on an enlarged and improved plan, with the aid of international co-operation, and asks for suggestions as to the best methods of inaugurating such a scheme.

Although this report deals with chemistry, it may be proper to mention here an important undertaking in another branch of science, as it affords an additional instance of the progress now making towards international co-operation in bibliography. At the Washington meeting of the International Congress of Geologists, a Committee on the Bibliography of Geology was appointed for the purpose of preparing a list of the geologic bibliographies now in existence. This work is now approaching completion under the direction of M. Emmanuel de Margerie (Paris), the Secretary of the International Committee.

American botanists also are showing their appreciation of bibliographical work. A Committee of the Torrey Botanical Club publishes in the *Bulletin* of the Club an "Index to recent Literature relating to American Botany." This index was begun in January, 1894, and is continued each month; the arrangement is alphabetically by authors.

At the Chicago Congress of Chemists, a Committee was appointed to bring about the organisation of a triennial (or quinquennial) International Meeting of Chemists. Prof. Frank W. Clark, one of the members of your Committee, is Chairman of that body. Perhaps the future World's Chemical Congresses may arrange the publication of an exhaustive Index to the Chemical Literature of the World by international co-operation, either in accordance with the scheme proposed by your Chairman in his Address at Chicago, or in some more efficient way.

Thus, it is evident that immense progress is being made in the compilation of indexes and bibliographies in many branches of science, in both Europe and America; it is to be hoped that American chemists, who have been in some measure pioneers in the matter, will feel stimulated to still greater exertions than before.

The Chairman has a limited number of copies of the Tenth Report containing a list of forty-five Indexes to Chemical Literature, which he will be glad to send to applicants. Communications should be addressed to the Chairman, at the University Club, New York City.

Committee:—

H. Carrington Bolton, Chairman,
F. W. Clarke,
Albert R. Leeds [in Europe],
Alexis A. Julian,
John W. Langley,
Albert B. Prescott [in Europe],
Alfred Tuckerman.

RECENT PUBLICATIONS RELATING TO CARBOHYDRATES.*

By W. E. STONE, Purdue University.

(Continued from p. 107).

Hexoses.

Some new occurrences of *dextrose* have been noted. Iridin, a glucoside from the roots of iris, yields glucose on inversion (*a*); another glucoside occurs in madder which forms a pentacetyl derivation, and on inversion is split into rubiadin and dextrose. The observer ventures the theory that in such glucosides the dextrose exists as an anhydride of a hepta-hydric alcohol (*b*). Dextrose results as one of the products of inversion of the gum in the fruit

* *Agricultural Science*, viii., No. 2.

of *Gymnocladus canadensis* (*c*). The pectin substance of pears is converted into dextrose on inversion (*d*). A reference to the occurrence of dextrose and levulose in leaves will be found among the physiological notes.

Phlorose, a sugar mentioned in the literature as derived from phloridzin, but of somewhat doubtful identity, has been shown to be nothing else than dextrose (*e*).

By melting together the salts (chloride, nitrate, and sulphate) of amido-guanidin with dextrose, lævo-rotatory compounds containing equal molecules of each are formed (*f*). Glucose-phenylhydrazon, upon more careful study, is found to be formed slowly when the dextrose has been long in solution, but rapidly with freshly dissolved dextrose. The compound is soluble in water and shows an increasing multirotation. $(\alpha)_D$ ten minutes after solution = $-15{\cdot}3°$; twelve hours after solution = $-46{\cdot}9°$. These properties are also thought to indicate the anhydride formula for dextrose (*g*).

Equal molecules of dextrose and barium or strontium hydroxides acting upon each other in solution produce a precipitate which presently goes into solution (*h*).

Glucose (and lactose) are said to give a reddish or brownish colouration when heated in alkaline solution with sodium nitro-prussiate (*i*). The fermentation of glucose by *Citromycetes pfefferianus* and *C. glabra* produces citric acid (*j*).

Invert sugar, when heated with lime water under the conditions of the saturation process in the clarification of beet juices, forms a compound, apparently a salt. The action upon levulose seems more intense than upon dextrose. The compound is inactive and without effect upon Fehling's solution. Upon decomposition volatile acids are distilled off (*k*).

Galactose is formed by inversion of the watery extract from certain lichens (*Cetraria islandica*, *C. nivalis*, and *Cladonia rhangiferina*). By direct oxidation with nitric acid, mucic acid results. No other sugars were obtained (*l*). Galactose phenylhydrazon is soluble in water and possesses the specific rotation $(\alpha)_D = -216°$ without multirotation (*m*).

In general the action of alkalis upon the glucoses is to convert them into saccharins. In a closer study of the action of calcium hydroxide upon galactose, it appeared that the continued action of the same at ordinary temperature for some weeks produced the normal or meta-saccharin in considerable quantity (14 per cent), and in the mother-liquor from this was found an isomer forming no crystallinic salts and no hydrazide, called para-saccharin. Upon reduction with hydriodic acid, meta-saccharin forms normal caprolactone and para-saccharin, (α)=ethyl-butyrolactone (*n*).

Mannose has been obtained from the coffee bean in addition to the other carbohydrates already mentioned (sucrose, galactose, pentose). Of these sugars only the sucrose exists in the bean, the others being derivatives of amorphous bodies there present (*o*).

Rhamnose, which has been found to be a methyl pentose (xylose), forms a phenylhydrazon, soluble in cold water with the specific rotation $(\alpha)_D = -54{\cdot}2°$ without multi-rotation. The specific rotation of the free sugar varies with the solvent. The hydrate reduced to water-free sugar, in watery solution shows $(\alpha)_D = -3{\cdot}6°$ at first, and $+9{\cdot}2°$ as the final constant (*p*).

Disaccharides.

Sucrose occurs in Cassava amounting to 17 per cent of the dry matter (*q*); in the fruit pods of *Gymnocladus canadensis* amounting to 15 per cent of the dry matter (*r*); it has also been noted among the other soluble sugars in germinating barley. The amount increases from 2·72 to 6·28 per cent simultaneously with the decrease of the starch, which the author regards as confirmatory of Brown and Morris's theory that under certain conditions starch may be converted into sucrose (*s*).

Thermal observations upon the solution of calcium oxide in sucrose solutions indicate that only the mono- and di-calcium saccharates are formed at ordinary temperature. The addition of 1 molecule of calcium oxide produces an increase of temperature equivalent to 7·2 cal. Two molecules increase the temperature to 11·7 cal. Beyond this point no addition of calcium oxide to the sucrose solution produces effect. If now, more sucrose be added, a supersaccharate results, and the temperature rises until 3 molecules of sucrose have been added, corresponding to the formula $C_{12}H_{22}O_{11}.CaO,3C_{12}H_{22}O_{11}$ (*t*).

Sucrose in solution is inverted by ferric oxide, which in turn becomes dissolved. This action does not occur, however, in alkaline solution (*u*). By the action of nitric acid upon sucrose, hydrocyanic acid is evolved (*v*).

If sucrose be heated for some time at 190°—200° it loses 10 per cent of its weight, and the residue is soluble in water; by longer heating a portion becomes insoluble, and the soluble portion when separated by dialysis is tasteless and neutral in reaction, with the composition expressed by the formula $C_{12}H_{18}O_{16}$. It has no longer the properties of a carbohydrate. By warming or long standing the molecular weight decreases and the substance seems to correspond to the caramel of Gelis. The undialysed portion resembles the caramel of Graham (*w*). By the action of caustic potash a considerable proportion of sucrose may be converted into acetone; by heating forty-six hours at 150°—200°, forty-six per cent of acetone is formed (*x*).

The inversion of sucrose by yeast in the process of fermentation may be regarded as a kind of chemical process capable of expression by a curve, and any condition which restrains the activity of the yeast diminishes the inversion (*y*). The slimy fermentation of sucrose produced by a species of *Leuconostoc* occurring sometimes in sugar factories, yields lactic acid as one of the products (*z*).

Maltose occurs in leaves as one of the products of assimilation (*aa*). In malt it amounts to about 51 per cent of the dry matter (*bb*). Maltose carboxylic acid obtained by the action of hydrocyanic acid upon maltose is an amorphous body which by hydrolysis breaks up into dextrose and α-gluco-heptonic acid (*cc*).

Lactose has been at times regarded as of a variable nature, according to its source, but specimens prepared from milk of cows, woman, ass, mare, goat, sheep, and dog and subjected to a careful comparative examination gave the same constants, viz., molecular weight, form of crystals, specific rotation, reducing power, and density, and were all regarded as identical (*dd*). Enzymes (rennet, trypsin, and pepsin) have no effect upon lactose at 40—55°, but its rotation is changed by heating (*ee*). The lactose carboryclic acid obtained from lactose nitril is soluble with difficulty, and on hydrolysis yields galactose and α-gluco-heptonic acid (*ff*). As a qualitative reaction for lactose (and glucose) heating in sodium solution with nitro-prussiate gives a reddish brown colour (*gg*).

Trehalose is found in certain fungi. In *Sclerotina tuberosa*, *Phallus impudicans*, and *Boletus satanas*, collected at different stages of development, the trehalose was wholly lacking in the younger growth, appeared just before the development of the fruit, and was wanting in the spore-bearing parts (*hh*). Trehalose upon inversion yields only dextrose, and the inversion is complete in five hours with 5 per cent sulphuric acid. Trehalose resembles maltose except that it does not reduce Fehling's solution nor form an osazone (*ii*). Trehalose is not susceptible to the action of diastase, emulsin, or invertin; by the action of *Aspergillus nigra* it is broken up into dextrose (*jj*).

Melezitose has been obtained in "honey dew" secreted on leaves of trees; it is estimated that 40 per cent of the "honey dew" consists of this rare sugar (*kk*).

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(ee) H. D. Richmond, *Analyst*, xvii., 222.
(ff) O. Reinbrecht, *Annalen d. Chem.*, cclxxii., 197.
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(ii) E. Winterstein, *Berichte der Chem. Gesell.*, xxvi., 3094.
(jj) E. Bourquelot, *Comptes Rendus*, cxvi., 826.
(kk) Maquenne, *Ibid.*, cxvii., 127.

(To be continued).

NOTICES OF BOOKS.

Bad Air and Bad Health. By Harold Wager and The Hon. Auberon Herbert. (With two Appendices.) London: Williams and Norgate. 1893 and 1894.

It has been sarcastically said in Germany that the two dominant ideas of the normal Englishman are the ventilation of his house and the conversion of the Chinese. The latter of these great tasks fortunately does not fall within our cognisance. In the former, despite lectures and essays innumerable, John Bull's success has not been complete. Hence the work before us is by no means an *Ilias post Homerum*.

The mischief has been demonstrated over and over again by the most eminent authorities, but it is not yet fully recognised in practice. Not alone in the cellar-dwellings of our great cities, and in the one-roomed abodes of the East End, but in our public conveyances, the air is too often intolerably bad. We have repeatedly seen, with little edification, how, when a train has disgorged its passengers in some great station, the porters at once carefully shut all the windows, although the same carriages are to be again occupied in less than half an hour. We frequently see in a tram-car, in addition to the lawful complement of passengers, an extra row standing between the seats and others crowding the conductor's platform, to the exclusion of any fresh air. In short, if the Black Death should ever again visit us, we have now arrangements for its distribution such as London of old never dreamt of.

But our authors do not merely collate and emphasize the testimony of such men as Ransome, Brunton, Klein, Russell, Collie, and others; they endeavour to show how the air of over-crowded dwellings, barracks, theatres, troop-ships, chapels, &c., produces disease. It is not, they show, merely the reduction of the oxygen below its normal limits, nor the accompanying increase of carbonic acid, which does the mischief. There is evidently some morbific agent at work over and above the diminished oxygen and the increased carbonic acid. This is known because gaseous mixtures, containing an amount of carbonic acid (artificially prepared) larger than we find in the air of over-crowded and ill-ventilated dwellings and work-rooms, produce no such serious results as does the latter. What is this additional something is still an open question. It has not yet been isolated and analysed; but in face of the experiments here recorded, and in face of the experience of daily life, it seems impossible to deny the presence, in the air of ill-ventilated rooms, of some organic compound or compounds which can scarcely be other than pathogenic, whether they are given off from the lungs or from the skin.

Some writers, indeed, question the necessity of good ventilation, on the faith of the good health and vigour of rabbits, rats, beavers, and other hybernating and burrowing animals. To this view we may oppose the opinion of Prof. Michael Foster, that each animal has its special coefficient of oxygen. Thus the dog consumes more oxygen per pound of its weight than the rabbit, and man again more than the dog. It may even be that some human races require more oxygen than others. Thus the Germans live and work with brain and muscle in atmospheres which an average Englishman regards as intolerably stuffy.

A correspondent of the authors makes the dry remark: —"I generally observe that where scientific men mostly congregate, the air is worse than elsewhere." But to keep up thorough ventilation in a country whose yearly average temperature falls short of 50° F. is certainly a hard battle, seeing that to many persons that temperature is the minimum at which life is worth living.

Some of the uncertain points here touched upon call for more investigation. If our results in the laboratory, chemical or physical, are doubtful, we do not renounce experiment, but multiply it under the most varied conditions, and in the end we arrive at the truth. Certain passages in this otherwise admirable treatise are, we fear, open to be perverted by the "anti" interests to their own ends. As to Kingsley's "wild north-easter" we cannot think it a *bona fide* utterance; it stands probably on the same plane as James Thomson's eulogy on early rising, thought out in bed.

The Discovery of Oxygen. Part I. Experiments by Joseph Priestley, LL.D., F.R.S. (1775). Edinburgh: W. F. Clay. London: Simpkin, Marshall, Hamilton, Kent, and Co., Ltd. 1894.

This volume forms one of the series of "Alembic Club Reprints," issued by Mr. Clay. The book is interesting as throwing a light not merely on the habits of thought and the chemical views of Priestley himself, but on the chemical world in general prior to the epoch of Lavoisier. Phlogiston, its presence or absence in any substance, its elimination or introduction in any reaction, was everything and explained everything. It was more even than oxygen became in the system of Lavoisier and his immediate disciples. But before we condemn the phlogiston-

olators—if we may coin such a word—let us reflect that, perhaps, our successors in the pursuit of Science may have occasion to correct us of a similar aberration. Priestley here tells us that he had formerly regarded atmospheric air as "*a simple elementary substance*, indestructible and unalterable, at least as much so as water is supposed to be." The gas which he obtained by heating mercuric oxide, or, as he named it, *mercurius calcinatus*, he concluded to be between five and six times as good as the best common air that he had ever met with (p. 19). He has no doubt that "atmospherical air, or the thing that we breathe, consists of the nitrous acid and earth, with so much phlogiston as is necessary to its elasticity." Still it was all the same "dephlogisticated air" or "pure air."

Expatiating on the possible medical uses and sanitary value of his "dephlogisticated air," he makes the very irrelevant remark:—"A moralist, at least, may say that the air which Nature has provided for us is as good as we deserve."

In view of Priestley's obstinate adherence to the phlogistian system, the following passage is of interest:—"We may take a maxim so strongly for granted that the plainest evidence of sense will not entirely change, and often hardly modify, our persuasions; and the more ingenious a man is, the more effectually he is entangled in his errors, his ingenuity only helping him to deceive himself by evading the force of truth."

A future part is announced on the experiments of Carl Wilhelm Scheele.

CORRESPONDENCE.

A SUPPOSED NEW GASEOUS ELEMENT IN THE ATMOSPHERE.

To the Editor of the Chemical News.

Sir,—There is one point which Prof. Dewar seems to have overlooked in his letters to the *Times* which you reprint in the Chemical News, vol. lxx., p. 87, namely, is it not possible to prepare this gas by using nitrogen from other sources than the atmosphere? If so, this would settle the question as to its being allotropic nitrogen. Again, is it possible to convert this gas into ordinary nitrogen? for if Prof. Dewar argues from analogy with phosphorus, surely it should be possible to convert it back again, as can be done with phosphorus. The density of the residual gas left by absorbing the oxygen and impurities in the air is heavier than the density of prepared nitrogen; therefore either allotropic nitrogen exists in the air in the free state, or it is not nitrogen in any form.

The importance of the subject of this letter must be my apology for trespassing on your valuable space.—I am, &c.,

Interested.

BLUNDERS IN MEDICAL CHEMISTRY.

To the Editor of the Chemical News.

Sir,—I have read with much interest Mr. Folkard's able paper in your last issue; he has struck an important note, and I trust that his remarks will reach all practitioners who have a kind of superstitious belief in drugs of the chemistry of which they know little or nothing, and of the physiological action still less. But there is one point in his paper which should be set right: it is where he says—"There is, however, one great consolation for the uric acid and pyæmia patients who have been wrongly treated, viz., that both lithia water and chlorate of potash are (so far as we know) harmless."

This is far from being the case, as I have more than once shown in my *Journal of Medicine*. Chlorate of potash, long considered harmless, is perhaps one of the most insidious of drugs. Prof. Jacobi, of New York, was, I believe, the first to show that, in large doses, or long-continued small doses, it gave rise to nephritis (kidney disease, albuminuria), and the deaths of several children in Belgium, to whom the supposed harmless chlorate of potash had been administered by some Sisters of Charity, to which I also called attention at the time, have not yet, apparently, opened the eyes of the general practitioner to the insidious nature of that compound. With regard to lithia water, like other alkaline preparations its long-continued use to ward off uric diathesis may produce phosphatic calculus.

The dangerous ignorance of the chemistry of drugs to which Mr. Folkard alludes is the bane of therapeutics, and it is to combat its effects that the veteran Prof. Burggreave, of Ghent University, has striven ardently for many years advocating chiefly the use of a small number of alkaloids in minute doses, repeated until the desired therapeutic effect is produced, and laying down strict rules by which the patient is ensured against any deleterious action on the part of the medicament—*primo non nocera*, as Hippocrates said.—I am, &c.,

T. L. Phipson.

The Casa Mia Laboratory,
Putney, S.W.

THE PROTECTION OF TRADE MARKS IN GERMANY.

To the Editor of the Chemical News.

Sir,—A new Law for the Registration and Protection of Trade Marks has been promulgated in Germany and comes into force on the 1st October next. This law, in its main provisions as to what constitutes a Trade Mark and is registerable as such, conforms very nearly to the Trade Mark section of the English Patent Law of 1883. It also embodies provisions analogous to some in the Merchandise Marks Act of 1887, which traders who send goods into Germany would do well to make themselves acquainted with. Any person who knowingly or through gross carelessness applies the name or firm of another party, or a Registered Trade Mark, is liable for damages, and further to a heavy fine or to six months imprisonment. Anyone who wrongfully applies a State Coat of Arms, or Coat of Arms of a District, or of a Municipal or Corporate body, for the purpose of creating confusion regarding the nature or value of the goods, or any person who offers for sale goods bearing such marks, will be punishable by fine or imprisonment. Foreign products which wrongfully bear the name and locality of a German firm, or a Registered Trade Mark, on entering Germany as imports, or for transit, are liable to seizure by the Custom House Authorities and confiscation. When an illegal mark on the goods cannot be removed, the goods may be destroyed. Where German goods must bear a certain mark or signification on being imported into a foreign country, to indicate that they are of German origin, or if such goods are not so favourably treated at the Custom House in respect of the Trade Marks, as the goods of other countries, the Federal Council is empowered to subject goods imported into Germany from such foreign countries to the same restrictions, and in case of violation thereof to seize and confiscate the goods. All Trade Marks at present registered in Germany must be re-registered under the new law within the next four years, *i. e.*, before the 1st October, 1898: there is no necessity, however, for any immediate action on the part of the proprietors of such Marks, but at the same time no advantage is gained by postponing it.—We are, &c.,

W. P. Thompson & Co.

6, Bank Street, Manchester,
August 21st, 1894.

THE ATOMIC WEIGHT OF CARBON.

To the Editor of the Chemical News.

SIR,—The *smallest* portion of carbon by which consecutive members of hydrocarbons can increase is 12; therefore the atomic weight of carbon is 12 and not 6. If carbon did equal 6 the next member to the body expressed by the formula $C_{15}H_{15}$ would certainly be $C_{16}H_{16}$, but the next member is not $C_{16}H_{16}$, but $C_{17}H_{17}$, and therefore the atomic weight of carbon must be 12.

I wrote a paper holding that by taking oxygen = 7, "*the atomic weight of the elements are expressed by natural numbers*" (see CHEMICAL NEWS, vol. lxx., p. 37). There being no element between carbon and nitrogen, no element between nitrogen and oxygen, and no element between oxygen and fluorine, and the combining values changing by 1 unit, it is very probable that the nitrogen atom contains 1 unit of matter more than the carbon atom, the oxygen atom contains 1 unit of matter more than the nitrogen atom, and the fluorine atom contains 1 unit of matter more than the oxygen atom.

I have since found that Mr. Newlands wrote in 1878 in the CHEMICAL NEWS (xxxvii., p. 255) showing that, by referring the atomic weights to sodium = 10, they come out approximately to ordinal numbers. This would give the atomic weight of carbon as 11·43, taking oxygen as 16, and would explain the anomaly found by Mr. J. A. Wanklyn in the vapour density of hydrocarbons if carbon is taken as 12.

Formula and density if carbon = 12.		Density found.	Diff.	Formula and density if carbon = 11·43.	
$C_{7\frac{1}{2}}H_{15}$ ..	3·63	3·69		3·72	C_8H_{16}
			0·39		
$C_{8\frac{1}{2}}H_{17}$ ..	4·11	4·08		4·19	C_9H_{18}
			0·41		
$C_{9\frac{1}{2}}H_{19}$ ..	4·59	4·59		4·66	$C_{10}H_{20}$
			0·43		
$C_{10\frac{1}{2}}H_{21}$ ..	5·08	5·02		5·12	$C_{11}H_{22}$
			0·49		
$C_{11\frac{1}{2}}H_{23}$ ..	5·56	5·51		5·59	$C_{12}H_{24}$
			0·57		
$C_{12\frac{1}{2}}H_{25}$ ..	6·04	6·08		6·06	$C_{13}H_{26}$
			0·45		
$C_{13\frac{1}{2}}H_{27}$ ..	6·52	6·53		6·52	$C_{14}H_{28}$

—I am, &c.,

EWART MATTHEWMAN.

Huddersfield.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxix., No. 7, August 13, 1894.

New Researches on the Infra-Red Region of the Solar Spectrum.—Prof. Langley.—(See p. 114).

Crystals Collecting on the Surface of a Solution Lighter than Themselves.—Lecoq de Boisbaudran.—If we place fragments of a substance heavier than the solution, some near the surface and others at the bottom of a saturated solution of the substance, it is observed that, thanks to the daily fluctuations of temperature, the upper fragments do not tend to disappear, whilst the lower fragments increase. This effect is commonly produced when the solution is not merely saturated with the substance of the fragments, but is besides saturated, or approximately saturated, with other substances. Still this is not always the case, as it appears from the following experiment. We saturate water at first and simultaneously with sodium carbonate and thiosulphate at about 20°. We then saturate the solution at the same temperature with crystalline sodium monosulphide, of which it dissolves considerable quantities. The liquid is then poured into a hydrometer-jar (from 0·10 to 0·15 metre in depth, at the bottom of which we place a certain quantity of crystalline Na_2S. We further place a very small fragment of Na_2S upon a support very little below the surface of the liquid. After the lapse of some days or some weeks all the Na_2S is collected upon the upper support, around the fragment which has been placed there. It is to be remarked that crystalline Na_2S is heavier than the complex solution. This effect may be explained by admitting for the solution containing the three salts of sodium a density inferior to that of the two salts, carbonate and thiosulphate.

Specific Heat of Liquid Sulphurous Acid.—E. Mathias.—The specific heat of liquefied gases has hitherto been little studied. Regnault's experiments on this subject were lost in 1870. Subsequently there have been made merely four determinations by Nadejdine (*Exner's Repertorium*, 1884), on liquid sulphurous acid between −20° and +10° and some determinations on ammonia between 26° and 46° made by Ludeking and Starr (*Silliman's Journal*, 1893). In a general manner the specific heat of liquids increases at the same rate as the temperature. What happens at the critical temperature? Theory (Raveau, Duhem) indicates that it increases indefinitely in absolute value, but remains positive, whilst under the same conditions the specific heat of saturated vapour is infinitely great, but negative. Experiment shows that the true specific heat of the liquid is always positive and increases constantly and indefinitely.

On Benzoilquinine.—A. Wunsch.—Prof. Schutzenberger has obtained a series of the benzoic derivatives of the alkaloïds by treating them with benzoic chloride. He has thus obtained benzoilquinine, which he describes as a resinous, uncrystalline mass. The author, on repeating his experiment, has obtained it crystallised in very definite colourless prisms. It is insoluble in water even at 100°. It dissolves very freely in alcohol, benzene, chloroform, petroleum ether, carbon disulphide and ether, which dissolves it better when saturated with water than when dry. The crystals are anhydrous and melt at 139° without decomposition. Their composition corresponds to the formula $C_{20}H_{23}(C_6H_5CO)N_2O_2$. Benzoilquinine if pure gives, like quinine itself, a green colouration with chlorine water and ammonia. The dilute aqueous solutions of its salts are fluorescent. The author has examined the hydrochlorates (basic and neutral), and the basic salicylate, tartrate, and succinate.

Journal fur Praktische Chemie.
New Series, Vol. xlix., Nos. 10 and 11, 1894.

Examination of Suberon.—W. Markownikoff.—Suberon is a pale yellow liquid having a somewhat impure odour of menthol. Its boiling-point is at 178°—179° (at an atmospheric pressure of 750 m.m. Its sp. gr. = 0·949. It dissolves readily in various solvents, but it is almost insoluble in water, although hygroscopic. Its composition corresponds to the formula $C_{17}H_{12}O$.

Researches from the Laboratory of the University of Freiburg in Breisgau.—These researches comprise a discussion by Ad. Claus of stereo-isomerism and the so-called stereo-chemical isomerism. The stereo-chemical theory is proving very fruitful in controversy of a somewhat acrimonious character. We have, further, C. Willgerodt's "corrections" of the views of Victor Meyer on iodoso and iodo compounds.

Calorimetric Researches by F. Stohmann.—This 31st memoir, by F. Stohmann and H. Langbein, discusses the thermic processes accompanying the formation of certain aminic acids and nitriles.

Notice on Paraoxybenzoic Methylester.—C. H. von Hoessle.—The ester may be obtained either by means of

concentrated sulphuric acid, of hydrochloric acid, or by the action of methyl iodide upon the silver salt of para-oxybenzoic acid suspended in alcohol.

A Correction.—J. W. Brühl.—The author wishes to rectify some inaccuracies occurring in his table to be found in this journal, New Series, vol. xlix., p. 263.

A Reply to H. C. Duisburg.—P. Heermann.—A question of priority.

Note on Phenylisoazolonimid.—The Editor.—A question of priority.

Part 12.

Researches from the Laboratory of the University of Freiburg.—These researches comprehend a memoir by Claus on the constitution of benzol, criticising a paper of J. W. Brühl in favour of the formula of Kekulé, and a paper of Ad. Claus and K. Reinhard on parabromquinoline.

Behaviour of certain Benzol Derivatives with Nascent Bromine.—W. Vaubel.—A continuation from former issues.

Preparation of Quinolins.—J. Walter.—The author heats the nitrobensene to ebullition in a round flask provided with a reflux glass tube and a dropping funnel, and if the warm mixture of glycerin, aniline, and sulphuric acid is added drop by drop the violent initial action of Skraup's process is avoided.

Condensation of Aldehyds with α-Naphthohydroquinone and α-Naphthoquinone.—J. Wurgaft.—A preliminary communication.

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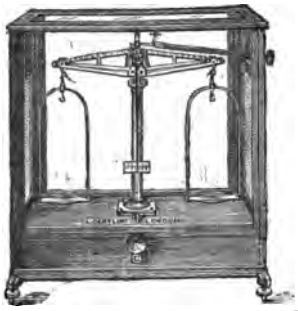

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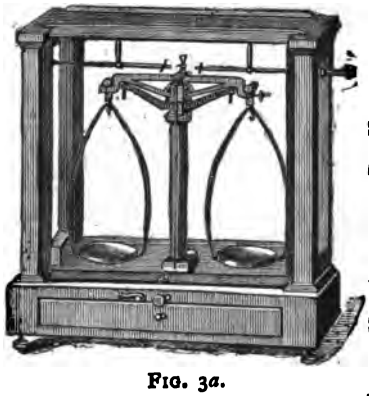

FIG. 3*a*.

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THE CHEMICAL NEWS.

Vol. LXX., No. 1816.

(STUDENTS' NUMBER).

ADDRESS TO STUDENTS.

The requirement of original research from candidates for the degree of D.Sc. at the London University is an experiment which we have watched with anxious interest. It was, indeed, but a small departure from the routine of cram and examinationism which presses like a nightmare upon our British seats of learning. It was a small step in the right direction, but we hoped that others might follow, and that Oxford, Cambridge, Dublin, the Victoria, &c., might be induced to adopt it. So far, we need scarcely say, we have watched and waited in vain. The London University has made no further movement, and even the Victoria is holding back.

The jubilant outcry raised over the success of Miss Fawcett at Cambridge convinced us how strong, in despite of arguments and facts, is the hold which examinationism still has upon public opinion, or rather upon public prejudice. It may, indeed, be that other seats of learning are awaiting the result of the introduction of research at the London University.

We are therefore sorry to learn from correspondence that the system is not working smoothly,—we do not say in principle, but in details. Perhaps there are especial difficulties to be encountered at a University like that of London, which is purely and essentially examinational. The following features of the present system are felt to be unsatisfactory:—

1. There is no standard laid down and maintained. Consequently some scope is given to the idiosyncracies and prepossessions of the examiners.

2. The dissertations given in are handed over to two examiners. Thus the examiner is still "lord of the ascendant." The question is raised whether two examiners are sufficient. We ask, in addition, whether it might not be an improvement if a number of specialists, not connected with the London University, were called in as assessors?

3. There is at present no obligation to publish the D.Sc. work *as such* in the scientific journals, and the London University is not obliged to exhibit or supply copies of theses, whether accepted or rejected. In consequence the determination of the standard of performance is almost impossible.

4. Cases should be distinguished:—

a. Whether the work is done with or under the guidance of a Professor, and contributed as a D.Sc. thesis.

b. When an assistant is employed.

c. When the work is done by the candidate without any direction.

It is complained that, contrary not only to common sense and even to the very letter of the regulations, it is possible for a candidate to be met with simple rejection, the reasons given in writing being, it is alleged, beside the real question.

We submit that the publication of the theses, with the mention of their acceptance or rejection, would prevent all perfunctory decisions on the part of the examiners, and furnish a court of appeal.

This subject is of the more urgent importance in view of the probable establishment of a London University which shall do something beyond mere examining in the Chinese style. We submit that the production of any valuable addition to the existing sum total of human knowledge should be accepted not merely as supplementary to, but as superseding the results of any examination. One great point in University reform should be, we submit, the establishment of independent distinct curricula. As Mephistophiles says, when, disguised in Faust's professorial gown, he is giving advice to a freshman, "Waehlt euch eine facultät"—Select your faculty.

We need scarcely say that we shall be happy to receive communications on the introduction of actual research as a necessary feature in our Universities, and on the necessary arrangements and conditions.

UNIVERSITIES AND COLLEGES.

UNIVERSITY OF LONDON.

Candidates for any Degree in this University must have passed the Matriculation Examination. No exemption from this rule is allowed on account of Degrees obtained or Examinations passed at any other University. This and all other Examinations of the University, together with the Prizes, Exhibitions, Scholarships, and Medals depending upon them, are open to Women upon exactly the same conditions as to Men.

There are two Examinations for Matriculation in each year; one commencing on the second Monday in January, and the other on the second Monday in June.

Any candidate who may obtain a place in the Honours Division at the Matriculation Examination in January is admissible to the Intermediate Examination either in Arts or in Science in the following July.

Intermediate Examination in Science.

The Intermediate Examination in Science will be held on the third Monday in July.

No candidate (with the exception of such as have obtained Honours at the Matriculation Examination in the preceding January) is admitted to this Examination within one academical year of the time of his passing the Matriculation Examination.

The Fee for this Examination is £5.

Examination for Honours.

Candidates for Honours in Chemistry will be examined in Inorganic Chemistry, treated more fully than in the Pass Examination. In addition, they will be examined practically in Simple Qualitative Analysis. This Examination will consist of six hours' examination by two printed papers and of six hours' practical work.

In the Examination for Honours, the Candidate, not being more than 22 years of age at the commencement of the Pass Examination, who most distinguishes himself will receive an Exhibition of £40 per annum for the next two years.

B.Sc. Examination.

The B.Sc. Examination will be held on the third Monday in October.

Candidates for this Examination are required to have passed the Intermediate Examination in Science at least one academical year previously.

The Fee for this Examination is £5.

Examination for Honours.

The examination for Honours in Chemistry will take

place on Monday, Tuesday, and Wednesday in the week following the Examination for Honours in Mathematics; on Monday by printed papers (chiefly on Organic Chemistry), and on Tuesday and Wednesday by practical examination in Qualitative and Quantitative Analysis.

The candidate, being not more than 23 years of age, who most distinguishes himself in Chemistry, will receive £50 per annum for the next two years, with the style of University Scholar.

DOCTOR OF SCIENCE.

The examination for the Degree of Doctor of Science takes place annually within the first twenty-one days of June.

No candidate is admitted to the examination for the Degree of D.Sc. until after the expiration of two Academical Years from the time of his obtaining the Degree of B.Sc. in this University.

Every candidate for this Degree must state in writing the special subject within the purview of the Faculty of Science, as set out in the Programme of the B.Sc. Examination, upon a knowledge of which he rests his qualification for the Doctorate; and with this statement he shall transmit an original Dissertation or Thesis (at least six copies), printed, type-written, or published in his own name, treating scientifically some special department of the subject so stated, embodying the result of independent research, or showing evidence of his own work, whether based on the discovery of new facts observed by himself, or of new relations of facts observed by others, or, generally, tending to the advancement of Science. Every candidate may further specify any printed contribution or contributions to the advancement of Science which he has at any time previously published. If the Dissertation or Thesis be approved by the Examiners, the candidate shall be required to present himself at the University upon such day or days within the first twenty-one days of June as may be notified to him, and shall, at the discretion of the Examiners, be further tested, either orally or practically, or by printed questions or by all of these methods, with reference both to the special subject selected by him and to the Thesis.

PRELIMINARY SCIENTIFIC (M.B.) EXAMINATION.

This Examination takes place twice in each year,—once, for Pass and Honours, commencing on the third Monday in July; and once for Pass Candidates only, commencing on the third Monday in January.

No candidate shall be admitted to this Examination unless he shall have passed the Matriculation Examination. Not less than five weeks before the commencement of the Examination he must apply to the Registrar for a Form of Entry, which must be returned not less than four weeks before the Examination, accompanied with the candidate's fee.

The Fee for this examination is Five Pounds.

UNIVERSITY OF OXFORD.

Waynflete Professor of Chemistry.—W. Odling, M.A., F.R.S.

Every Student must reside in one or other of the Colleges or Halls, or in licensed lodgings, for a period of three years, passing at least two examinations in Arts, and one in either Mathematics, Natural Science, Law, Modern History, or Theology, when, if he obtain a first, second, or third class, he can take his B.A. Degree; if he do not gain such honour he has to pass a third examination in *Literis Humanioribus*.

The fee for students working in the Laboratory for three days in the week during the Term is £3; for students working every day, £5.

Scholarships of about the value of £75 are obtainable at Christ Church, Magdalen, and other colleges, by competitive examination in Natural Science.

More detailed information may be obtained from the University Calendar; the Examination Statutes, 1893; the Student's Handbook to the University; and from the professors.

UNIVERSITY OF CAMBRIDGE.

Professor of Chemistry.—G. D. Liveing, M.A., F.R.S.

Jacksonian Professor of Natural and Experimental Philosophy.—J. Dewar, M.A., F.R.S.

The Student must enter at one of the Colleges or Hostels, or as a Non-collegiate Student, and keep terms for three years by residence in the University. He must pass the previous examination in Classics and Mathematics, which may be done in the first or third term of residence, or, through the Oxford and Cambridge Schools Examination Board, or through the Senior Local Examinations, before commencing residence. He may then proceed to take a Degree in Arts, either continuing mathematical and classical study, and passing the ordinary examinations for B.A., or going out in one of the Honour Triposes.

The scholarships, ranging in value from £20 to £10 a year, are chiefly given for mathematical and classical proficiency. Scholarships are given for Natural Science in Trinity, St. John's, St. Peter's, Clare, Christ's, Sidney, Pembroke, Caius, and Downing Colleges; the examinations being in December, at Easter, and in June and October.

The Chemical Laboratory of the University is open daily for the use of the Students. The Demonstrators attend daily to give instructions. A list of the lectures is published annually, in June, in a special number of the *Cambridge University Reporter*, which may be had from the Cambridge Warehouse, in Paternoster Row, or through any bookseller.

Non-collegiate Students are allowed to attend certain of the College Lectures and all the Professors' Lectures, and have the same University status and privileges as the other Students. Full particulars may be obtained by forwarding a stamped directed envelope to the Assistant Registrar, Cambridge, or from the *Cambridge University Calendar*.

UNIVERSITY OF DUBLIN.

TRINITY COLLEGE.

Professor of Chemistry.—J. Emerson Reynolds, D.Sc. M.D., F.R.S.

Assistant Lecturer.—Emil A. Werner, F.C.S., F.I.C.

Demonstrator.—William Early, F.I.C.

The general Laboratories include working accommodation for 120 Students, and the Quantitative and Research Laboratories for about 40 Students. The Laboratories will open on the 1st of October. Lectures will commence about November 1st.

The Laboratories and the Lectures of the Professor of Chemistry can now be attended by Students who do not desire to reside in the University or proceed to its Degrees.

The full Course of General and Analytical Chemistry occupies three years, but a Student is free in his third year to devote most of his time to a special department of Pure or Technical Chemistry. Students can enter for any portion of the Course. The following Lectures are delivered:—

1. *Inorganic Chemistry and Chemical Philosophy.* — Elementary, first year; advanced, second year.
2. *Organic Chemistry.* — General, second year; advanced, third year.
3. *Metallurgy.*—A Course for Engineering and Technical Students.

The Laboratories are open every day from 10 to 5 o'clock (except Saturdays, when they close at 1 o'clock).

The Summer Course of Practical Chemistry for Medical Students begins during the first week in April and terminates with the first week in July.

The University of Dublin grants the Degree of Doctor of Science to graduates of Master's standing whose independent researches in any branch of Science are of sufficient merit.

KING'S COLLEGE.

(Division of Engineering and Applied Science).

Professor of Chemistry.—J. M. Thomson, F.C.S.

Demonstrators of Practical Chemistry.—G. S. Johnson, F.C.S., and Herbert Jackson, F.C.S.

Students of the First Year are admitted to the Course of Theoretical and Applied Chemistry. The Course commences with a View of the Forces which concur to the production of Chemical Phenomena, after which the laws of Chemical Attraction are discussed, and the Non-metallic elements and their principal Compounds are described. The Metals and their principal compounds are next examined, care being taken to point out the applications of the Science to the Arts; and the processes of the different Manufactures and of Domestic Economy are explained and illustrated. Examinations of the Class, both *viva voce* and by written papers, are held at intervals during the course at the usual Lecture hour.

Second Year.—Students attend in the Laboratory twice a week, and they go through a course of Manipulation in the most important operations of Chemistry, including the first steps of Analysis. Any Student of this Division may be admitted to this Class at any period of his study on payment of an extra fee.

Experimental and Analytical Chemistry in the Laboratory.—The object of this Class is to afford to Students who are desirous of acquiring a knowledge of analysis, or of prosecuting original research, an opportunity of doing so under the superintendence of the Professor and Demonstrator; Students may enter, upon payment of extra fees, at any time except during the vacation, and for a period of one, three, six, or nine months, as may best suit their convenience. The laboratory hours are from ten till four daily, except Saturday, on which day the hours are from ten till one.

In addition to the Laboratory Fee, each Student defrays the expenses of his own experiments. The amount of this expense, which is comparatively trifling, is entirely under his own control.

Special hours and fees are arranged for the convenience of such Third Year Students as wish to study Analytical Chemistry.

Fees.—Chemistry per term, £3 3s. 0d.; per ann., £8 8s. 0d.; Practical Chemistry per term, £4 4s. 0d.; per ann., £10 10s. 0d.; Experimental and Analytical Chemistry—Daily attendance: One month, £4 4s.; Three months, £10 10s.; Six months, £18 18s.; Nine months, £26 5s. Three days a week: One month, £2 12s. 6d.; Three mo.s, £6 6s.; Six mos., £11 11s.; Nine mos., £15 15s.

Rules as to Admission of Students.

I. The Academical Year consists of Three terms: Michaelmas Term, from beginning of October to the week before Christmas; Lent Term, from the middle of January to the week before Easter; Easter Term, from Easter to the beginning of July.

II. The days fixed for the Admission of New Students: in the Academical Year 1894-95, are Tuesday, October 2, Wednesday, January 16, and Wednesday, April 24.

Metallurgy.

Professor.—A. K. Huntington, F.I.C., F.C.S., &c.

The following subjects are treated of in the Lectures: The Selection and Economic Preparation of Fuel and of Refractory Materials; the methods by which metals are obtained from their ores, and the means by which they are rendered suitable for the various requirements of the Arts.

Particular attention is paid to the study of the Nature and Properties of Metals and Alloys available for Constructive Purposes.

In the Metallurgical Laboratory, which is always open during College hours, the relation between the Chemical Composition of Metals and their Mechanical Properties may be studied by the aid of Testing Machinery.

Photography.

Lecturer.—Prof. J. M. Thomson, F.R.S.E., F.C.S.

Arrangements are made for a complete Course of Instruction in Photography to the students of the third year. A glass house has been erected, and in connection with it a Laboratory for the preparation of Photographic Chemicals. Students entering to this department will be afforded every facility for practising the Art in all its branches.

In addition to the regular College Course in Photography occasional classes are formed, consisting each of about six gentlemen, who meet twice a week. The fee for private instruction is £5 5s. for ten lessons, or £10 10s. for three courses. There is in every case a charge of £1 each course for chemicals.

Evening Classes.

Classes for Evening Instruction in various subjects are held during the months from October to March, inclusive, and during the months of April, May, and June.

UNIVERSITY COLLEGE.

Faculty of Science.

Professor.—William Ramsay, Ph.D., F.R.S.

Assistant Professor.—J. N. Collie, Ph.D.

Assistants.—Alexander Kellas, B.Sc., and Morris Travers, B.Sc.

The Session is divided into three Terms, as follows, all the dates being inclusive:—

First Term, from Tuesday, October 2nd, until Friday, December 21st;

Second Term, from Tuesday, January 15th, 1895, till Friday, March 29th;

Third Term, from Tuesday, April 23rd, till Friday, June 28th. Class Examinations begin on Monday, June 17th.

Junior Courses.

First Term: Tuesday and Thursday at 11, and Saturday at 10, commencing October 4, 1894. Third Term: Tuesday and Thursday at 10, Friday at 4, beginning April 23rd, 1895. Fee:—£4 4s.

These Courses will each consist of about thirty lessons, partly theoretical and partly practical, on the non-metallic elements. Frequent exercises will be given.

Senior Course of Chemistry.

First and Second Terms: The Class meets four times a week, on Mondays, Wednesdays, Fridays, and Saturdays, at 9, for Lectures, Examinations, and Exercises, commencing October 3rd.

Fee:—For the Course, £7 7s.; Perpetual, £9 9s.; for the First or Second Terms, £4 4s.

This Course and the Practical Class cover the subject as prescribed for the Preliminary Scientific (M.B.) and Int. Examination in Science of the University of London.

For the Preliminary Scientific Examination Students who take the three subjects for that examination in July attend during the First and Second Terms.

Advanced Course of Chemistry.

Second and Third Terms.—The class meets twice a week, on Tuesdays and Thursdays, at 9, beginning on January 15. The hour will be altered by special arrangement with the class if necessary.

Fee:—For the Course, £3 3s.; for a Term, £2 2s.

This Course will be found suitable for those about to proceed to graduation as Bachelor of Science in London University, and to those who intend to choose Chemistry as a profession. Such students should also work in the Laboratory during as many hours as they can spare.

Organic Chemistry.

Tuesday and Thursday, at 9, in the First Term, beginning October 4th; Tuesday, Thursday, and Saturday, at 10, in the Second Term; and Tuesday and Thursday at 9, and Saturday at 11, in the Third Term. The hour of meeting will be altered should the class desire it.

This Course of Organic Chemistry is intended for those who in studying the subject have not a Medical Examination chiefly in view. Candidates for Honours at the Int.M.B. are, however, recommended to attend this Course instead of the Special Summer Course.

The Course includes the subjects required at the B.Sc. Examination, Pass and Honours; but no previous acquaintance with Organic Chemistry will be expected of those joining the Class.

Fee:—For the Course, £6 6s.; for the Second and Third Terms, £4 14s. 6d.; for a Term, £2 12s. 6d.

Practical Class.

First and Second Terms, Tuesday and Thursday, at 11, commencing October 4th.

Fee, including cost of materials, £5 5s.; for a Second Course, £3 3s.

The Course includes the Practical Chemistry required at the Preliminary Scientific and Intermediate Science Examinations.

Senior Practical Class.

Wednesdays from 2 to 4 and Saturdays from 10 to 12 during the Third Term; also Tuesdays and Thursdays from 11 to 12.

Fee:—(Including cost of materials) £5 5s.; for a Second Course, £3 3s.

Analytical and Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., Saturdays excepted, from October until the middle of July, with a short recess at Christmas and at Easter.

Fees: for the Session, £26 5s.; six months, £18 18s.; three months, £10 10s.; one month, £4 4s.

Three specified days a week:—for the Session, £15 15s.; six months, £11 11s.; three months, £6 6s.; one month, £2 12s. 6d., exclusive of expense of materials. Students may enter at any period of the Session.

The Laboratory Course includes the Practical Chemistry required at the following Examinations of the University of London:—Prel. Sci. (M.B.), Intermediate M.B., Intermediate Science, B.Sc.

Students who wish to attend the Lectures on Chemical Technology may acquire here the requisite knowledge of Practical Chemistry and Analysis.

When accompanied by, or preceded by, attendance on the Lectures on Inorganic and Organic Chemistry, the Laboratory Course qualifies Students in the application of Chemistry to Manufactures, Metallurgy, Medicine, or Agriculture, &c.

There is also a Chemical Library containing the chief Journals and Standard Works on Chemistry.

Certificates of Honour are granted to competent Students on the work done during the Session. The Tuffnell Scholarship (£100 for two years) will also be competed for in the Session 1894-95; also the Clothworker's Scholarship of £30.

ROYAL COLLEGE OF SCIENCE AND ROYAL SCHOOL OF MINES.

Professor.—W. A. Tilden, D.Sc., F.R.S.

Assistant Professor.—W. P. Wynne, D.Sc., A.R.C.S.

Demonstrators.—H. Chapman Jones and A. E. Tutton.

Assistants.—G. S. Newth, J. W. Rodger, and W. Tate.

The Royal College of Science at South Kensington is intended, primarily, for the instruction of teachers, and of students of the industrial classes selected by competition in the examinations of the Science and Art Department. The Royal School of Mines is incorporated with the Royal College of Science. Students entering for the Associateship of the School of Mines obtain their general scientific training in the Royal College of Science. The instruction in the Royal College of Science is arranged in such a manner as to give the Students a thorough training in the general principles of Science, followed by advanced instruction in one or more special branches of Science. The Associateship is granted in certain divisions or lines of study. Students who go through any one of the prescribed courses of instruction and pass the necessary Examinations receive a Certificate of Associateship of the Royal College of Science, or of the Royal School of Mines. Students who are not candidates for the Associateship are permitted to take up the course of instruction in one or more special branches of science, and on passing the examination receive a Certificate to that effect. The Associateship of the Royal College of Science is given in one or more of the following divisions:—Mechanics, Physics, Chemistry, Biology, Geology, and Agriculture, and the Associateship of the Royal School of Mines in Metallurgy and Mining.

The course of instruction, which lasts for three years, is the same for all the divisions during the first year, after which it is specialised in accordance with the Scheme detailed in the Prospectus of the School.

The Session is divided into two Terms. The first Term begins on the 3rd of October and ends about the middle of February. The second Term begins in the middle of February and ends about the middle of June.

Examinations are held at the end of each course of instruction and at such other periods as may be found necessary. On the results of these examinations the successful candidates are arranged in two classes, first and second. There are also "Honours" examinations for the subjects of the third year, the successful candidates being placed in order of merit. A student obtains the Associateship who passes in all the subjects of the first two years and in those of the special division he selects for his Associateship. A student who goes through the prescribed course of instruction in any subject and passes the final examination in it receives a certificate to that effect.

Students who do not wish to attend the lectures are admitted for short periods to the laboratories, at the discretion of the Professors. The fees for the laboratories are £4 per month.

Students not entering for the Associateship are admitted to any particular course of study, so far as there is room, on payment of the fees shown in the following table:—

	Lectures.	Laboratory.
	£	£
Chemistry	3	13
Physics	5	12
Biology with Botany	5	12
Geology with Mineralogy ..	4	8
Mechanics	4	6
Metallurgy	2	13
Mining	4	
Astronomical Physics	2	3

Agricultural Chemistry, per term, £13. Mathematics and Mechanical Drawing, £3 per term. Freehand Drawing, £1 per term.

The fees for the first two years amount to about £75, and for the remainder of the course for the Associateship they vary from £30 to about £40.

Both the private and the State-aided students are required to furnish themselves with certain instruments and apparatus before the commencement of the course. These are enumerated in the syllabuses of the several subjects.

Officers of the Army, Navy, and Civil Service, recommended by their respective Departments, are admitted to the Lectures and Laboratories at half fees.

Associates of the Royal College of Science or of the Royal School of Mines have the privilege of free admission to the Library and to all the courses of lectures.

Bona fide teachers qualified to earn payments for teaching Science according to the rule of the Science Directory may obtain permission to attend free any course of lectures.

Several valuable Exhibitions, Scholarships, and Prizes are attached to the studentship.

Summer Courses for Teachers.—Short courses of instruction are given annually, about July, in different branches of science for the benefit of teachers of science schools in the country. The courses last three weeks. About 250 teachers are admitted to them, and they receive 3rd class railway fare to and from South Kensington, and a bonus towards their incidental expenses of £3 each. (See Science Directory.)

Working Men's Lectures.—Notification of these will be given in the newspapers.

THE SCHOOL OF THE PHARMACEUTICAL SOCIETY OF GREAT BRITAIN.

The Fifty-third Session will commence on Monday, October 3rd, 1894. Entries not previously arranged with the Dean or Secretary may be made between 10 a.m. and 1 p.m. on that day.

Professors and Lecturers.—Prof. Dunstan, M.A., F.R.S., Sec. C.S., F.I.C., Chemistry; Prof. Attfield, Ph.D., F.R.S., F.I.C., Practical Chemistry; Prof. Green, M.A., B.Sc., F.L.S., Botany (Dean); Prof. Greenish, F.I.C., F.L.S., Materia Medica; Mr. Joseph Ince, F.L.S., Pharmacy and Practical Pharmacy.

A Course of Lectures on Physical, Inorganic, and Elementary Organic Chemistry commences in October and terminates at the end of March. An Advanced Course of Lectures on Organic Chemistry begins in April and extends to the end of June. The lectures will be given at 9.30 a.m. These Lectures are adapted to the requirements of Pharmaceutical and Medical Students, and also those who are proceeding to degrees at the University of London, or who are preparing for the examinations of the Institute of Chemistry.

Entries may be made for single classes. A bench in the chemical laboratories, which are open daily throughout the Session, can be engaged for any period. Certificates of attendance at the two Courses of Lectures on Chemistry and at the Chemical Laboratories are accepted as evidence of chemical training by the Institute of Chemistry in connection with the Examinations for the Associateship, and also by the conjoint Board of the Royal Colleges of Physicians and Surgeons, as well as by other examining bodies.

Prospectuses and further information may be obtained from Mr. F. W. Short, B.Sc., Secretary to the School, 17, Bloomsbury Square, London, W.C.

UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH.

University of Wales.

Professor.—H. Ll. Snape, D.Sc. (Lond.), Ph.D. (Gœttingen), F.I.C.

Assistant Lecturer and Demonstrator.—A. W. Warrington, M.Sc. (Vic.), F.I.C.

Assistant Lecturer in Agricultural Chemistry.—J. Alan Murray, B.Sc. (Edin.).

The College is open to male and female students above the age of sixteen years. The Session commences on Saturday, September 29, on which day all Students will be expected to meet the Professors in the Library of the College.

Lecture Courses.—(1) Matriculation Course; three lectures weekly during the Michaelmas and two weekly during the Lent and Easter Terms. (2) Intermediate Science Pass Course; three lectures weekly during the Lent and Easter Terms. (3) Intermediate Science Honours Course; two lectures weekly during the Lent and Easter Terms. (4 and 5) B.Sc. Pass and Honours Courses; each three lectures weekly throughout the Session. (6 and 7) Courses in Agricultural Chemistry. For students in their first year, 3 lectures, and for those in their 2nd year, 2 lectures weekly throughout the Session.

Laboratory Courses.—The Laboratory is open daily from 10 a.m. to 1 p.m., and from 2.15 to 5 p.m., except on Saturdays. Classes for the Systematic Study of Qualitative and Quantitative Analysis will be formed, and Special Courses will be arranged for those who intend to follow Medicine or Pharmacy, or any one particular branch of Applied Chemistry, always provided that such Students possess the requisite knowledge of Theoretical Chemistry. The hours will be arranged, as far as possible, to suit the requirements of the individual Student.

The College is recognised by the Royal University of Ireland, and by the Colleges of Physicians and Surgeons of England, Scotland, and Ireland as an institution at which the instruction necessary for their respective Diplomas in Medicine, in Chemistry, Physice, and Biology may be given. One year for graduation in Medicine and two years for graduation in Science may be spent at Aberystwyth.

Fees.—The Fee for the whole Session, if paid in advance, is £10; if paid by Single Terms, for the first term of attendance in each Session, £4; for the second term, £3 10s.; for the third term, £3. These composition fees enable the Student to attend any or all the Classes of the College, with the exception that a small extra fee is charged for Laboratory Instruction. Thus, for Practical Chemistry, the additional fee is, for six hours' work per week, 10s. per term, and for twelve hours, 20s. per term. The fees for those who desire to spend several days weekly in the laboratory may be learned on application to the Registrar. Fee for a single Lecture Course £1 per term.

Scholarships and Exhibitions varying in value from £10 to £40 per annum will be offered for competition at examinations which commence on September 18, and exhibitions are awarded at the end of the Session on the results of the class examinations.

The Chemical Laboratories in connection with this College have been recently built, and are fitted with every convenience for the prosecution of chemical studies.

Intending Students requiring further information are recommended to write to the Registrar for a copy either of the General Prospectus or of one of the Special Prospectuses issued for the Agricultural and Normal Departments.

UNIVERSITY COLLEGE OF NORTH WALES, BANGOR.

Chemistry.—Professor, James J. Dobbie, M.A., D.Sc. Demonstrator, Fred. Marsden, Ph.D., B.Sc. Assistant Lecturer in Agricultural Chemistry, F. V. Dutton.

Physics.—Professor, Andrew Gray, M.A., F.R.S.E.

The Session opens October 2nd, 1894. All regular classes are open to men and women students above the age of 16 years. The following Courses of Lectures will be given.

Matriculation Course.—Subjects: Those prescribed for the London University Matriculation Examination. Fee for the Term £2 2s. A class for revision of Matriculation Work will be held during the Summer Term. Fee for the Term, £1 1s.

Intermediate Course. — Inorganic Chemistry and Elementary Physical Chemistry. Fee for the Term £2 2s.

B.Sc. Course.—Organic Chemistry. Fee for the Session, £3 3s.

Medical Course.—Inorganic and Organic Chemistry. Fee for the whole Course, £4 4s.

Agricultural Chemistry.—Fee, £2 2s.

Laboratory Courses.—The laboratory is open on five days of the week from 10 a.m. to 4 p.m. for instruction in Chemical Analysis and in the Application of Chemistry to Medicine and the Industrial Arts. Fees: six hours per week, £1 1s. per Term; twelve hours, £2 2s.; eighteen hours, £3 3s.; twenty-four hours, £4 4s. Composition Fee for all Laboratory Classes of the Intermediate Science Course taken in one year, £4 4s.

The Chemistry, Botany, Zoology, and Physics Courses are recognised for Medical graduation in the Universities of Edinburgh and Glasgow, and students can make one *Annus medicus* at the college. The Science Courses are recognised for part of the science degree course of the University of Edinburgh.

UNIVERSITY COLLEGE OF SOUTH WALES AND MONMOUTHSHIRE, CARDIFF.

Professor.—C. M. Thompson, M.A., D.Sc., F.C.S.

Demonstrator.—E. P. Perman, D.Sc., F.C.S.

The Session commences October 8th, and terminates on June 28th, and is divided into three terms.

The Junior Course (delivered during the Michaelmas term only) consists of about 50 lectures, and will cover the subjects prescribed for the London University Matriculation examination. Fee, £2 2s. A revision class is held in the Summer term.

The Intermediate Course consists of 50 lectures held during the Lent term in continuation of the Junior Course, and, together with laboratory practice and the course on Chemical Theory, will cover the subjects required for the Intermediate Examination in Science and the Prel. Sci. (M.B.) Examination of the University of London. Fee, £3 3s.

A course of about 20 lectures on the Theory of Chemistry will be given during the summer term.

The Senior Course consists of some 90 lectures devoted to Organic Chemistry; Fee, £3 3s.

A course of 30 lectures on Qualitative and Quantitative Analysis will also be given.

In the laboratory each student works independently, so that the course of study may be adapted to the requirements of the individual. Hours, 9 to 1 and 2 to 5; Saturday, 9 to 1. Fees—Six hours per week, £3 3s. per session; twelve hours, £2 2s. per term; eighteen hours, £3 3s. per term; twenty-four hours £4 4s. per term.

Registered medical students can prepare for the Intermediate M.B. Examination of the University of London, and spend three out of their five years of medical study in Cardiff. Medical students wishing to graduate at a Scottish University, or preparing for a Conjoint Board Surgical and Medical Diploma, or for the Diploma of the Society of Apothecaries, can spend two years in Cardiff. For further information see the prospectus of the Faculty of Medicine, which may be obtained from the Registrar.

The College is recognised as an institution at which two years of the course for the degree of Bachelor of Science of the University of Edinburgh may be spent.

Students by making a payment of £10 at the commencement of each session may compound for all lecture fees for the whole session. Laboratory fees are not included in the composition fee, but Students preparing for the Science Examinations of the University of London may, by making a payment of £13 13s. at the commencement of each Session, compound for both Lecture and Laboratory Fees during the Session.

At the entrance examination in September, and the annual examination in June, several scholarships and exhibitions are awarded. Great importance is attached to special excellence in one subject.

The College Prospectus and also further information as to scholarships, may be obtained from the Registrar.

A Hall of Residence for Women Students is attached to the College.

UNIVERSITY COLLEGE, BRISTOL.

Professor of Chemistry.—Sydney Young, D.Sc., F.R.S.
Lecturer.—Arthur Richardson, Ph.D.

The session 1894-95 will begin on October 4th. Lectures and classes are held every day and evening throughout the Session. In the Chemical Department lectures and classes are given in all branches of theoretical chemistry, and instruction in practical chemistry is given daily in the chemical laboratory. The department of experimental physics includes various courses of lectures arranged progressively, and practical instruction is given in the physical and electrical laboratory. The Department of Engineering and the Constructive Professions is designed to afford a thorough scientific education to students intending to become engineers, or to enter any of the allied professions, and to supplement the ordinary professional training by systematic technical teaching. This department includes courses specially arranged for students intending to become civil, mechanical, electrical, or mining engineers, surveyors, or architects. Those who attend the mechanical engineering course enter engineering works during the six summer months, and, in accordance with this scheme, various manufacturing engineers in the neighbourhood have consented to receive students of the College into their offices and workshops as articled pupils at reduced terms. Medical education is provided by the Faculty of Medicine of the College. Several Scholarships are tenable at the College. Full information may be obtained from the Secretary.

Day Lectures.

Inorganic Chemistry.

The Courses treat of the principles of Chemistry, and of the Chemistry of the Non-Metals and Metals.

Junior Course.—Two Lectures a week will be given during the First and Second Terms.

Senior Course.—Three Lectures a week will be given throughout the Session.

Advanced Course.—One Lecture a week will be given throughout the Session.

Organic Chemistry.

This Course will relate to the more important groups of the Compounds of Carbon.

Two Lectures a week will be given during the Second Term, and three Lectures a week during the Third Term. Fee, £3 3s. An advanced course of lectures will also be given one day a week during the session.

Practical Chemistry.—Laboratory Instruction.

The Laboratory will be open daily from 10 a.m. to 5 p.m., except on Saturdays, when it will be closed. Instruction will be given in the Laboratory in all branches of Practical Chemistry, including Qualitative and Quantitative Inorganic and Organic Analysis, the preparation of Chemical Products, and Inorganic and Organic Research. Special facilities will be afforded to those who desire to study Practical Chemistry as applied to the different processes employed in the Arts and Manufactures. The Laboratory is under the immediate supervision of the Professor and the Lecturer. Fees in Guineas—

	5 Days a Week.	4 Days a Week.	3 Days a Week.	2 Days a Week.	1 Day a Week.
Per Session	15	12½	10	7½	5
,, Two Terms ..	11	9	7½	5½	3½
,, One Term ..	7	6	4½	3½	2½

Students may arrange to divide their days of laboratory work into half-days.

Chemical Scholarship.—Among others, a Chemical Scholarship of £25 is offered for competition.

Evening Lectures.

Two courses of Lectures will be delivered during the First and Second Terms; they will be devoted to the consideration of the general Principles of Chemistry and Chemical Physics and the Chemistry of Non-Metallic and Metallic Elements. Special attention will be paid throughout to those products which have a practical application in the Arts and Manufactures. Fee for each course, 7s. 6d.

University College, Bristol, has been approved by the Council of the Institute of Chemistry as a College at which all the subjects required for the admission of Associates to the Institute are taught.

MASON COLLEGE, BIRMINGHAM.

Professor.—Percy F. Frankland, Ph.D., B.Sc., F.R.S.
Assistant Lecturer.—C. F. Baker, Ph.D., D.Sc.

The Session will be opened on Monday, October 1st, 1894.

Elementary Course.

Forty Lectures adapted to the requirements of beginners will be given in the Winter and Spring Terms. A Second Course of Twenty Lectures, having reference only to the subjects included in the syllabus of the Matriculation Examination of the University of London, will be given in the Summer Term. Lecture days—Wednesdays and Fridays at 11.30, Thursdays at 3.30.

Persons entirely unacquainted with Chemistry are recommended to attend the first of these Courses before entering for the General Course, which commences in October. Candidates for the Matriculation Examination of

the University of London are advised to attend both these Courses.

General Course.

The General Course of Lectures on Chemistry will be found useful by Students who are afterwards to become Engineers, Architects, Builders, Brewers, or Manufacturers (such as Metallurgists, Alkali, Soap, Manure, Glass, or Cement Makers, Bleachers and Dyers, &c.)

Students preparing for the Intermediate Examination in Science and Preliminary Scientific (M.B.) Examination of the University of London should attend the Lectures on Inorganic Chemistry (Winter and Spring Terms).

Candidates for Intermediate Examinations in Medicine will in general require only that part of the course (Summer Term) which relates to Organic Chemistry.

The full course, extending over three terms, will also satisfy the requirements of Students preparing for the Associateship of the Institute of Chemistry, so far as attendance at lectures on General and Theoretical Chemistry is concerned.

1. From October to March (Winter and Spring Terms). About eighty lectures on Inorganic Chemistry and Chemical Philosophy will be given on Mondays, Tuesdays, Wednesdays, and Thursdays from October to December, and on Mondays, Tuesdays, and Wednesdays from January to March, at 9.30 a.m. A Tutorial Class is held in connection with this Course once a week throughout the Session. Fee, £5 5s. for the course.

2. April to June (Summer Term). About thirty lectures will be given on Elementary Organic Chemistry, or the chemistry of the most important series of carbon compounds. This course will include all the subjects required for the Intermediate Examination in Medicine of the University of London. Lecture Days—Monday, Wednesday, and Friday at 9.30 a.m. Fee, £1 11s. 6d.

Advanced Course.

An Advanced Course for the study of Theoretical Chemistry and those parts of the subject which are required for the degree of B.Sc. in the University of London will meet twice a week. Fee for the session, £3 3s.

Laboratory Practice.

The College Laboratory is open daily from 9.30 to 5, except on Saturdays, when it is closed at 1 p.m.

Candidates for Intermediate Examination in Science, Preliminary Scientific (M.B.), B.Sc., and Intermediate Examination in Medicine of the University of London, may obtain in the Laboratory of the College the instruction necessary. The three months Course of Practical Chemistry for the B.Sc., Edinburgh, in the department of Public Health, may be taken in the Mason College Laboratory. Fees :—

	All day.	Three hours per day.
One Term	7 guineas	.. .. 4½ guineas.
Two Terms	13 „	.. .. 8½ „
Three Terms	18 „	.. .. 12 „

A Course of short demonstrations and exercises is given by the Professor or one of his Assistants once a week. All first-year Students are required to attend, unless exempted for special reasons by the Professor. No Fee.

Metallurgy.

Three Courses of Ten Lectures will be given on the Principles and Practice of Metallurgy. Fee, 10s. 6d. for each of the first two courses, and for each section of the third course. A more advanced course upon selected subjects is also given by Mr. McMillan, the Lecturer in Metallurgy.

There is a separate laboratory for metallurgical students in which provision is made for instruction in assaying, &c.

Evening Classes.

Several Courses of Evening Lectures are arranged during the Winter and Spring Terms of each session. The subjects are treated in a less technical manner and the fees are nominal.

Excursions.

During previous Sessions permission has been obtained to visit some of the great factories in or near Birmingham, in which chemical and metallurgical industries are carried on. Students have thus had most valuable opportunities of gaining a practical acquaintance with some branches of Applied Science. The privilege thus courteously granted by several manufacturers will, it is hoped, be enjoyed in every future Session. The excursions will be conducted by the Professor or Lecturer.

BRADFORD TECHNICAL COLLEGE.

Chemistry and Dyeing Department.

Professor.—Mr. Arthur Dufton, B.A. (Cantab.), B.Sc. (Lond.).

Demonstrator.—Mr. J. E. Shaw.

Lecturer on Botany and Materia Medica.—William West, F.L.S.

The school year is divided into three terms. The Session commences on September 18th and terminates on July 22nd. The course of instruction extends over two years, and embraces Lecture Courses on Inorganic and Organic Chemistry, the technology of the textile fibres, mordants, natural and artificial colouring matters, technical analysis, and laboratory practice in analytical chemistry, chemical preparations, and dyeing. Inclusive fee, £4 4s. per term.

During the first and second terms Evening Classes are held for the benefit of persons engaged during the day and for pharmaceutical students.

ROYAL AGRICULTURAL COLLEGE, CIRENCESTER.

Chemical Department.

Professor.—Prof. E. Kinch, F.C.S., F.I.C.

Assistants.—Cecil C. Duncan, F.I.C., and W. James.

Systematic courses of Lectures are given on the various branches of Chemistry in its relation to Agriculture, illustrated by experiments, and by the collections in the College Museum. They comprise the laws of Chemical Combination and the general Chemistry of mineral bodies, and of the more frequently occurring bodies of organic origin, with the relationships of their leading groups; and, finally, the applications to practical operations of the Chemistry of the atmosphere, of soils and manures, of vegetation and stock feeding, and of the processes and products of the dairy.

In the Laboratory practical instruction is given in the construction and use of apparatus and in Chemical manipulation and analysis, both qualitative and quantitative. After studying the simple operations and the properties of the commonly occurring substances, the Students are taught to analyse a series of compounds, and apply the knowledge thus obtained to the analysis of manures, soils, waters, feeding stuffs, dairy products, and other substances met with in the ordinary course of Agricultural practice. Chemico-agricultural researches are undertaken by the senior Students under the direction of the Professor and his Assistants.

VICTORIA UNIVERSITY. THE YORKSHIRE COLLEGE, LEEDS.

Professor of Chemistry.—Arthur Smithells, B.Sc. Lond., F.I.C.

Lecturer in Organic Chemistry.—Julius B. Cohen, Ph.D., F.I.C.

Assistant Lecturer in Agricultural Chemistry.—Herbert Ingle, F.I.C.

Demonstrators.—A. C. Wright, B.A., and T. Ewan, Ph.D., B.Sc.

The Session begins October 8, 1894.

Lecture Courses.

1. General Course of Chemistry.—Monday, Wednesday, and Friday, at 11.30 a.m., from October to the end of the second term, and during part of the third term. Fee for the Course, £4 4s.

2. Inorganic Chemistry.—First year Honours Course, Non-metals. Monday, Wednesday, and Friday, at 9.30 a.m. Fee, £3 13s. 6d.

3. Inorganic Chemistry. — Second year Honours Course, Metals. Tuesday, Thursday, and Saturday at 9.30 a.m. Fee, £3 13s. 6d.

4. Organic Chemistry. — Tuesday, Thursday, and Saturday at 12 noon Fee £3 13s. 6d.

5. Organic Chemistry Honours Course. — Wednesday and Friday at 12 noon. Fee, £2 12s. 6d.

6. Theoretical Chemistry.—Advanced Course. Tuesdays and Thursdays at 9.30 a.m. Fee, £2 12s. 6d.

7. Chemistry as Applied to Coal Mining.— Tuesday during the First Term, at 4 p.m.

8. Agricultural Chemistry.—Monday, Tuesday, and Friday, at 3 p.m., during first and second terms.

9. Chemistry for Teachers.—Saturdays from 9.30 to 12.30 in the first and second terms. Fee, £4 4s.

Laboratory Courses.

The College Laboratory will be open daily from 9 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it will close at 1 p.m.

Fees for the Session—Students working six days per week, £21; five, £18 18s.; four, £16 16s.; three, £13 13s.

Class in Practical Chemistry, Saturday mornings, from 9.30 to 12.30. Fee £1 11s. 6d.

Practical Chemistry for Medical Students.—Tuesdays, 9.30 to 11.30 October to end of December; Thursdays, 2 to 4 from January to end of March.

Practical Course in Sanitary Chemistry.—At times to be arranged.

Practical Organic Chemistry for Medical Students.—At times to be arranged.

Evening Class.

A Course of twenty Lectures by Mr. Ingle, on the Elements of Inorganic Chemistry (the Non-Metals) will begin during the first and second Terms, on Wednesdays, at 7.30 p.m., beginning October 10. Fee, 10s. 6d.

Dyeing Department.

Professor.—J. J. Hummel, F.I.C.

Lecturer and Research Assistant. — A. G. Perkin, F.R.S.E.

Assistant Lecturer.—W. M. Gardner.

This Course extends over a period of three years, and is intended for those who wish to obtain a full scientific and practical education in the art of dyeing. It is suitable for those who purpose in the future to take any part in the direction of the operations of dyeing or printing of textile fabrics, *e.g.*, the sons of manufacturers, calico printers, managers, master dyers, &c.

Leather Industries Department.

Lecturer.—H. R. Procter, F.I.C.

The full Course, which extends over a period of three years, is suitable to all who intend to become Technical Chemists in the Leather Industry, or managers of important works, and is recommended to sons of tanners. The Courseincludes instruction in chemistry, engineering, leather manufacture, and practical work in the Leather Industries Laboratory.

Agricultural Department.

Professor.—James Muir.

The full Course occupies two years, and includes instruction in chemistry, physics, botany, engineering and surveying, and the principles of agriculture, as well as practical work in the various laboratories and out-door agriculture.

Research Students are admitted to the College Laboratories on reduced terms.

Several valuable Scholarships are at the disposal of the College, viz., the Cavendish, Salt, Akroyd, Brown, Emsley, Craven, and Clothworkers' Scholarships, and the Leighton Trustees' Exhibition, and one of the new 1851 Exhibition Scholarships. The West Riding County Council Scholarships are tenable at the Yorkshire College.

UNIVERSITY COLLEGE, LIVERPOOL.

Professor.—J. Campbell Brown, D.Sc.

Lecturer on Organic Chemistry.—C. A. Kohn, B.Sc., Ph.D.

Lecturer on Technological Chemistry.—T. L. Bailey, Ph.D.

Demonstrators and Assistant Lecturers.—T. L. Bailey, Ph.D., C. A. Kohn, B.Sc., Ph.D., and S. B. Schryver, B.Sc., Ph.D.

Assistant.—H. H. Froysell.

The Session commences October 4th.

The Classes meet the requirements of candidates for the Ordinary B.Sc. Degree, for Chemistry Honours, or for the M.Sc. or D.Sc. Degree in Victoria University; for Degrees in Medicine of Victoria, London, and Edinburgh; for a special Technological Certificate of University College; and for those studying Chemistry as a preparation for professional, technical, or commercial life. The Classes qualify for the Fellowship of the Institute of Chemistry of Great Britain and Ireland, and other Examination Boards.

Lecture Courses.

General Elementary Course on the principal non-metallic elements and the most important metals, the principles of Chemical Philosophy, and an introductory sketch of Organic Chemistry. Three Terms. Fee, £4.

Engineer's Course of Lectures with Practical Class. Two Terms. Fee, £4.

Dental Course, Lectures and Practical. Fee, £5 5s.

Course A.—Non-metals. Fee, £3 10s.

Course B.—Metals. Fee, £3 10s.

Course C.—Organic Chemistry. Fee, £3.

Course H.—Special Organic Subjects. Fee, £1.

Course D.—Physical Chemistry. One Term. Fee, £1.

Course E.—History of Chemistry and of the Development of Modern Chemical Philosophy. Three Terms. Fee, £2.

Courses F.—Technological Chemistry and Metallurgy: Lectures on Technology are given in connection with Laboratory work at hours to be arranged. The subjects are varied in different years. (1) Alkali and Allied Manufactures. (2) Copper, Iron, and Steel. (3) Lead, Silver and Gold, Aluminium, and other Metals. (4) Distillation of Coal and Tar Industries. (5) Fuel and Gas. (6) Chemistry Applied to Sanitation. (7) Technical Gas Analysis. Three terms. Fee, each course £1 10s.

Practical Classes.

(1) Junior. (2) Intermediate: Qualitative Analysis of Inorganic Substances and of some of the more common Organic Substances. (3) Revision Class. (4) Senior: Practical Organic (Advanced Medical Class). (5) Practical Exercises on Technology, Pharmaceutical Chemistry, Saitanry subjects, Examination of Water and Air, of Animal Secretions, Urinary Deposits, Calculi, and Poisons. (6) Quantitative Class: Course arranged to suit the requirements of the London University B.Sc. Examinations, Pass and Honours, and for Intermediate M.B. Honours.

Chemical Laboratory.

The Chemical Laboratories provide accommodation for every kind of chemical work.

Students desirous of gaining a thorough theoretical and practical acquaintance with Technical Chemistry, or who intend to adopt Chemical work as a profession, must devote three or four years to special study.

TABLE OF FEES.

Per Week.	One Term, Three Months.	Three Terms, One Session.
One day	£4	£8
Two days	6	10
Three days	8	12
Four days	9	15
Whole week	10 10s.	21

Pharmaceutical Course, £12.

Technological Curriculum.

Preliminary Year.—Chemistry, the Elementary Course.

Practical Classes 1 and 2. Mathematics, or Mechanics, or Physics. Elementary Engineering, Drawing, and Design (in this or one of the following years). French or German. Or the Preliminary Course and Examination may be taken.

First Year.—Chemistry—Courses A and B; Chemical Laboratory three days per week; Practical Organic Class during the Summer Term; Technological Chemistry, Course F. Physics, with laboratory work, one day per week. Mathematics (intermediate). German; Intermediate B.Sc. Examination may be passed. Engineering, First Year Course, Autumn and Lent Terms.

Second Year.—Chemistry, Lecture Course on Organic Chemistry, C, Lecture Course E or D, Technological Chemistry, Course F. Chemical Laboratory, four days per week. Engineering, Mathematics, or Physics (Advanced). The Final Examination for the Victoria B.Sc., or the Intermediate Examination of the Institute of Chemistry, may be taken.

Third Year.—Courses D, F, and C. Any other Courses omitted in a previous year. Laboratory, five days per week. Students may finally choose a special subject either of research or of applied Chemistry. The Final Examination for the Associateship of the Institute of Chemistry of Great Britain and Ireland may be taken. Three years study after passing the Preliminary Examination of Victoria University are required for the B.Sc. Degree in the Honours School of Chemistry.

The Sheridan Muspratt Chemical Scholarship of £50 per annum, tenable for two years, will be competed for in December, 1894, on an Examination in subjects which are included in the first two years of the above curriculum. Other Scholarships, Entrance Scholarships, and Free Studentships are also available to Students.

Evening Classes.

Lectures will be given on Chemistry in relation to every-day Industries.

The Prospectus containing full particulars may be obtained from the Registrar, University College, Liverpool.

LIVERPOOL COLLEGE OF CHEMISTRY.

Principal.—George Tate, Ph.D., F.I.C., F.C.S.

The Laboratories are open daily from 10 to 5, excepting Saturdays, when they close at 1 p.m. The course of instruction is adapted to the requirements of students of Chemistry as a science, and in its applications to chemical and metallurgical industries. The fee for a three years' course of study is eighty guineas, or per session of three months eight guineas.

Prospectuses, containing full particulars of the day and evening classes, may be had on application at the College.

DURHAM COLLEGE OF SCIENCE, NEWCASTLE-ON-TYNE.

Professor of Chemistry.—P. Phillips Bedson, M.A., D.Sc., F.I.C., F.C.S.

Lecturer in Chemistry—Saville Shaw, F.C.S.

Lecturer in Agricultural Chemistry.—R. Greig Smith, B.Sc. (Edin.), F.C.S.

The Session will commence on September 24th, 1894.

1. *General Course.*—This Course of Lectures will extend over the three terms of the Session, and is intended to serve as an introduction to the Science. The Lectures will be of an elementary character, and whilst framed to meet the requirements of First Year Students will also be serviceable to such as intend pursuing Chemistry in its various applications in the arts and manufactures, as, for instance, Brewing, Metallurgy, the Manufacture of Soda, Soap, Glass, &c. The subjects treated will include an exposition of the Principles of Chemistry, and a description of the preparation and properties of the chief Elementary Substances, both metallic and non-metallic, and their more important native and artificial compounds. A section of this Course will be devoted to an outline of Organic Chemistry. The class will meet on Mondays, Wednesdays, and Fridays, at 11.15 a.m., and will commence on Wednesday, October 4th. Fee, £3 10s. for the Session.

2. *Advanced Course.*—Inorganic Chemistry, Tuesdays and Fridays, 3 to 4 p.m., during Michaelmas and Epiphany Terms.

3. *Organic Chemistry.*—A Course of about ninety Lectures will be given throughout the Session, the subject of which will be Organic Chemistry, or the Chemistry of the Carbon Compounds. This class will meet on Tuesdays and Thursdays, at 11 a.m., and will commence on Thursday, October 5th. Fee, £3 10s. for the Session.

Advanced Classes will be formed for the study of Inorganic, Organic, and Theoretical Chemistry. Fee for each course, £2 2s.

A Lecture Course in Analytical Chemistry will be given on Mondays, at 3 p.m., commencing October 8th. Fee, £1 1s.

Metallurgy and Assaying.—Lecturer, Saville Shaw, F.C.S. A Metallurgical Laboratory is provided, in which instruction is given in the ordinary processes of Dry-Assaying, and in the preparation and analysis of Alloys, &c. Fee as for Chemical Laboratory.

Agricultural Chemistry.—The instruction in this branch of Chemistry will consist of a series of Lectures and of special practical work in the Chemical Laboratory. Students will be expected to have a knowledge of Elementary Chemistry, such as may be obtained by attending the General Course.

The Lecture Course in Agricultural Chemistry is arranged for two days a week throughout the Session. Fee, Two Guineas.

Practical Chemistry.—The Laboratory is open from 10 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it closes at 1 p.m. *Laboratory Fees.*—Students working six days per week, £5 5s. per term; three days, £3 3s. per term, £8 8s. per session; two days, £2 2s. per term, £5 5s. per session; one day per week, £1 11s. 6d. per term, £3 3s. per session.

Courses of Study.—Students will be divided into two classes:—(1) Regular, or Matriculated Students, who are also Members of the University of Durham; and (2) Non-Matriculated Students. Regular Students will be required to follow such a course of study in the subjects professed in the College as will enable them to pass the Examinations for the title of Associate in Physical Science of the University of Durham. Non-Matriculated Students will attend such classes as they may select. Every candidate for admission as a matriculated student must pass an examination on entrance, in reading, writing from dictation, English or Latin Grammar, arithmetic (including decimals), and geography. Registered students in medicine are exempted from this examination, or students who produce a certificate of having passed either of the two following examinations:—

1. Durham Examination for certificate of proficiency in General Education, held in March and September.

2. Durham Examination for Students in Arts in their first year, or any examination of a similar nature that may be accepted by the Council.

Associateship in Physical Science.—Every candidate for the Associateship in Physical Science will be required to satisfy the examiners in—Mathematics, Physics, Chemistry, and either Geology or Natural History—in an examination to be held at the end of the candidate's first year. Associates in Science are admissible one year after obtaining the title of Associate to examination for the degree of Bachelor of Science of the University of Durham.

Exhibitions.—Three Exhibitions of the value of £25, £15, and £10 respectively will be awarded in October next to Candidates desirous of attending the first year course of study in the College.

The examination will be held at the College, and wil commence on Monday, September 24th.

Evening Lectures.—Courses of Evening Lectures will be given, with a Practical Class for Laboratory instruction.

Two Exhibitions of £15 each will be awarded at the next

examination of "Persons not members of the University," which will be held at Durham in March next.

Several other valuable Scholarships are available for students.

OWENS COLLEGE,
VICTORIA UNIVERSITY, MANCHESTER.

Professor and Director of the Chemical Laboratory.—Harold B. Dixon, M.A., F.R.S.

Professor of Organic Chemistry.—W. H. Perkin, Ph.D., F.R.S.

Demonstrators and Assistant Lecturers.—George H. Bailey, D.Sc., Ph.D.; Arthur Harden, M.Sc., Ph.D.; P. J. Hartog, B.Sc.; B. Lean, B.A., D.Sc.; and W. A. Bone, B.Sc., Ph.D.

Lecturer in Dyeing and Printing.—Ernest Bentz.

Assistant Lecturer in Metallurgy.—Gilbert J. Fowler, M.Sc.

The Session begins on October 2, 1894, and ends on June 23, 1895.

The instruction is given by means of Experimental Lectures and Tutorial Classes. The Chemical Classes form part of the Courses for Chemistry in the University.

General Chemistry.

General Chemistry Course.—Tuesdays, Thursdays, and Saturdays, at 9.30, during the two Winter Terms.

Introduction to Organic Chemistry.—Wednesdays and Fridays, at 9.30, during Lent Term.

These courses are intended for Medical Students and others beginning the study of chemistry.

First Year Honours Course.—Mondays, Wednesdays, and Fridays, 11.30 a.m., during the two Winter Terms. The Non-Metals.

Second Year Honours Course.—Mondays, Wednesdays, Fridays, 3.30 p.m., during the two Winter Terms. The Metals.

Third Year Honours Course.—At times to be arranged. Physical Chemistry.

Organic Chemistry (General).—Tuesdays and Thursdays, 9.30, during two Winter Terms.

Organic Chemistry (Honours).—Mondays and Fridays, 9.30, during the two Winter Terms.

History of Chemistry and Chemical Philosophy.—Wednesdays, 10.30, during the Session.

METALLURGY.—*Lectures*: The Metallurgy of Copper, Lead, Silver, Gold, and the Metallurgy of Iron and Steel will be given in alternate years. *Practical*: Saturdays, 9.30.

The Chemical Laboratories are open daily from 9.30. a.m. to 4.30 p.m., except on Saturdays, when they are closed at 12.30 p.m.

An ordinary degree of B.Sc. in Chemistry, Victoria University, may be taken at the College in three yeare. The Degree of B.Sc. with Honours in Chemistry can also be taken in three years, and the College Certificate in Technological Chemistry may be taken in the same time.

A number of important Scholarships, &c., are available to students.

Technological Chemistry.

First Course.—Sulphuric Acid and Alkali Manufactures. General Principles of Chemical Engineering.

Second Course.—The Chemistry of Fuel. The Manufacture of Illuminating Gas and Gaseous Fuel.

Third Course.—The Chemistry of Coal Tar.

Fourth Course.—Natural and Artificial Dye-stuffs.

Fifth Course.—Calico-printing.

Certificates in Applied Chemistry.

The course extends over a period of three years, and comprises systematic instruction by means of lectures and practical work in the laboratories.

Before admission to the first year's course students are required to give such evidence of elementary knowledge of Mathematics and Chemistry as shall be considered satisfactory by the Senate.

The first year's course is the same for all students working for the certificate.

In the second and third years a choice may be made between Inorganic and Organic Chemistry. By this division of the subject a student wishing to apply himself specially to the inorganic side of the science, may attend during his second year the Honours course in Metals, and courses on Geology or Mineralogy, and during his third year, courses on Metallurgy and on Geology or Mineralogy; while a student wishing to apply himself specially to the organic side of the science, may attend during his second and third years the Courses on Organic Chemistry, and courses on the Coal Tar Colours and on Dyeing and Printing.

Part of the Laboratory practice in the second and third years will consist in the examination and analysis of raw materials, products from chemical works, &c., in connection with the special courses of lectures on Applied Chemistry. In the Chemistry and Physical laboratories the practical work in the second year will be arranged in accordance with the branch of Chemistry selected by the candidate.

In the third year the student, if sufficiently advanced, will be set to work on some analytical process or problem in Applied Chemistry, under the direction of the teaching staff.

UNIVERSITY COLLEGE, NOTTINGHAM.

DEPARTMENT OF CHEMISTRY, METALLURGY, AND AGRICULTURE.

Professor of Chemistry.—Frank Clowes, D.Sc. Lond., F.I.C.

Demonstrators of Chemistry.—J. B. Coleman, A.R.C.Sc. Dublin, F.I.C., R. L. Whiteley, F.I.C., and M. E. Feilmann, B.Sc. Lond.

The Classes of the College are open to students of both sexes above sixteen years of age.

The dates of commencement and end of Terms in the Session 1894-95 will be as follows:—First Term, October 8th to December 22nd; Second Term, January 14th to March 30th; Third Term, April 17th to June 29th.

Lecture Courses.—The Chemistry Day Lectures extend over three years. In the first year a student enters for the course on Non-Metals for the first two terms and for Elementary Organic Chemistry in the third term. In his second year he takes the course on Metals for the first two terms. In his third year he attends a course on Advanced Organic Chemistry or Applied Chemistry. Fee for Day Lectures and Classes: Non-Metals or Metals 42s.; Organic Chemistry (one term) 21s.; Advanced Organic Chemistry, 21s. per term.

Demonstrations and Lectures on Analytical Chemistry will be given in the day and evening, and should be attended by all students.

A Chemical Calculation Class is also held. Fee per Term, 5s.

Students may qualify themselves by attendance at these lectures and classes for the Examinations of the Universities of London, Cambridge, or Oxford, and for the Medical Examinations of the Royal College of Surgeons and of the Universities of Cambridge and Edinburgh: they may also obtain instruction in Chemistry for technical or other purposes, and can enter for a full Chemical Engineering Curriculum. Special attention is given to the requirements of candidates for the Associateship of the Institute of Chemistry.

Practical Chemistry.—The chemical laboratory is open every day from 10 to 5, except on Saturday, when the hours are from 9 to 1, and on Thursday from 10 to 1, and on Tuesday and Thursday evenings from 7 to 9. Each Student works independently of other Students at a course recommended by the Professor. Instruction is given in general Chemical Manipulation and in Qualitative and Quantitative Analysis; and students are enabled to work out the applications of Chemistry to Pharmacy, Dyeing, Agriculture, Brewing, Iron and Steel, Tanning, and other Manufacturing Processes. Fees: For one term, £7; for the session, £18; for day students for six hours weekly 40s., and 5s. extra for each additional hour per

week. For evening students, 10s. for two hours per week, three hours 15s., four hours 20s., six hours 30s., per term.

Courses of Technical Chemistry Lectures are also given on Engineering, Dyeing and Bleaching, Brewing, Plumbing, Bread-making, Gas Manufacture, and on other processes of applied Chemistry.

Pharmaceutical Students can at all times work in the Chemical Laboratory, taking work suitable for the preparation for the Minor Examinations.

Government Lectures and Classes.—Evening Lectures and Laboratory instruction will be given by the Demonstrators of Chemistry to Students who intend to present themselves for Examination by the Government Science and Art Department in May next. Inorganic, organic, and practical chemistry, agricultural chemistry, and metallurgy will be taught in the elementary, advanced, and honours stages, each of which commences at the beginning of the College Session in October. Fee for each Lecture Course, 5s.; for each Laboratory Course, 10s.

An Agricultural Course of instruction, extending over two years, is now organised under the general direction of Mr. M. J. R. Dunstan, M.A., F.R.S.E. It includes instruction in chemistry, botany, agriculture, with practical work on experimental fields, dairy work, farriery, land surveying, &c. The instruction is designed for those who intend to become farmers, bailiffs, land agents, or colonists, and may be extended to a third year if desired. Fee, £15 per annum for residents in Notts, £20 to residents in other counties.

Full information concerning all College Classes is given in the College Prospectus, price one penny.

FIRTH COLLEGE, SHEFFIELD.

Professor of Chemistry.—W. Carleton Williams, B.Sc., F.C.S.

Demonstrators and Assistant Lecturers.—G. Young, Ph.D., and L. T. O'Shea, B.Sc., F.C.S.,

The Session will commence on October 1st.

First Year's Course.—Chemistry of the Non-Metallic Elements. Tuesday and Friday from 10 to 11 a.m. Fee, £2 12s. 6d.

Second Year's Course.—Chemistry of Metals. Monday and Thursday from 10 to 11 a.m. £2 12s. 6d.

Third Year's Course.—Organic Chemistry, on Wednesday, from 9 to 10, and Saturday, from 10 to 11. Fee, £2 2s.

Short Courses of Lectures are also given by L. T. O'Shea on Electrolytic Analysis, and on the Chemistry of Coal Mining.

A Course of Lectures is arranged for Medical Students, with a special class in Qualitative Analysis.

Laboratory.—Working hours to be arranged between Professor and Students.

Sessional Fees for Day Students:—Six hours per week, £5 5s.; Nine, £7; Twelve, £8 8s.; Eighteen, £11 5s.: Twenty-four, £14; Thirty-two, £17.

Day Students may not enter for less than six hours a week. Students joining the Laboratory at Christmas will be charged two-thirds and at Easter one-third of the Fees for the whole Session.

Fees for short periods (working thirty-two hours per week):—For one month, £3 3s.; two months, £5 5s.

An arrangement has been entered into with the Science and Art Department, South Kensington, which will enable Science Teachers to work in the Chemical Laboratory for three, six, or twelve hours a week on payment of one-quarter of the usual fee, the Department being willing to pay the remainder under certain conditions, of which full information may be obtained on application to the Registrar.

Students who have worked for three sessions in the Chemical Laboratory are eligible for election to a scholarship value £150 for two years.

Evening Classes.—Lectures, Wednesday, 8 to 9. Laboratory instruction, Wednesday, 6 to 9, and another series to be arranged if desired. Sessional Fee, one evening per week, £1 10s.; two, 5os.; or Lecture Class and Laboratory, on Wednesday evening, £1 10s.

UNIVERSITY COLLEGE, DUNDEE.

(University of St. Andrews).

Professor of Chemistry.—James Walker, Ph.D., D.Sc.

Assistant Lecturers.—F. J. Hambly, F.I.C., and J. R. Appleyard, F.C.S.

Lecture Assistant and Laboratory Steward.—J. Foggie, F.C.S.

The Winter Session begins on October 10th, and ends on March 21st. The Summer Session extends from May 1st to July 12th.

The First Year's Lecture Course on Systematic Chemistry is given daily during the Winter Session, and embraces the Elements of Inorganic and of Organic Chemistry.

Advanced Courses, of about fifty lectures each, will be given during the year as follows:—

Organic Chemistry; Inorganic Chemistry, including the more important technological applications; Theoretical and Physical Chemistry; Bleaching and Dyeing, including the Chemistry of the Textile Fibres.

Practical Instruction in all of the above branches will be given in the Laboratories and Dye-house. To supplement the Practical work of First Year's Laboratory Students a short course of Lectures on *Analytical Chemistry* will be offered. Special facilities are afforded to Research Students.

The Lectures and Laboratory Practice in Chemistry are recognised by the Medical Colleges of London and Edinburgh, as well as by the University of Edinburgh, for degrees in Science and Medicine. The Courses are suitable for the degrees of the University of London and for the Civil Service appointments, and will also satisfy the requirements of Students in Pharmacy, and of Students who intend to become candidates for the Associateship of the Institute of Chemistry, as far as qualification in Chemistry is concerned.

UNIVERSITY OF EDINBURGH.

Department of Chemistry.

Professor.—Alex. Crum Brown, M.D., D.Sc., F.R.S., Pres. C.S.

Assistants.—L. Dobbin, Ph.D.; H. Marshall, D.Sc.; W. W. Taylor, M.A.; and A. F. Watson, B.Sc.

The working terms are—Winter Session, from middle of October to middle of March; Summer Session, from beginning of May to end of July.

Lecture Courses.—During the Winter Session a General Course of Chemistry for medical and science students is given by the Professor. The class meets daily; fee £4 4s. A class for advanced students is held in summer: it meets thrice weekly; fee £2 2s.

In addition to the above, Lecture Courses are given by the Assistants on special subjects, such as Chemical Theory, Physical Chemistry, or some particular branch of Organic and Inorganic Chemistry. These lectures are free to Laboratory Students.

Tutorial classes are held in connection with the General Course.

Laboratories.—Practical classes for Medical Students meet daily during the latter part of the Winter Session and in the Summer Session. (Fee, £3 3s.) The laboratories for analytical and advanced practical work are open daily from 10 till 4. (Fees: Winter Session, £10 10s.; Summer Session, £6 6s.) Full Courses of instruction are given in Analytical, Practical Organic and Inorganic Chemistry. Facilities are afforded to advanced students who desire to undertake chemical investigations.

Various prizes and scholarships are attached to the laboratory and general class.

Graduation.—Two Degrees in Pure Science are conferred, viz., Bachelor of Scienc (B.Sc.) and Doctor of Science (D.Sc.).

Candidates for Degrees in Science, if not graduates (by examination) in Arts in one of the Universities of the United Kingdom or in a Colonial or Foreign University recognised for the purpose by the University Court, must pass a preliminary examination in (1) English; (2) Latin, Greek, French, or German; (3) Mathematics; (4) One of the languages Latin, Greek, French, German, Italian, not already taken under (2), or Dynamics. In the case of a student whose native language is other than European, the Senatus may, at the Preliminary Examination, accept such language as a substitute for a modern European language. The Senatus may also in such a case accept as an alternative to Latin or Greek any other classical languages, such as Sanscrit or Arabic.

The First B.Sc. Examination embraces Mathematics, or Biology (*i.e.*, Zoology and Botany), Natural Philosophy, and Chemistry. The Second B.Sc. Examination includes any three or more of the following subjects:—1. Mathematics. 2. Natural Philosophy. 3. Astronomy. 4. Chemistry. 5. Human Anatomy, including Anthropology. 6. Physiology. 7. Geology, including Mineralogy. 8. Zoology, including Comparative Anatomy. 9. Botany, including Vegetable Physiology. Chemistry in this examination includes Inorganic Chemistry, Organic Chemistry, Relation between Chemical and Physical Properties, Complex Qualitative Analysis (practical), Simple Quantitative Determinations (practical), and Gas Analysis (practical).

A candidate for the D.Sc. Degree must submit a thesis on original work done by him. The Thesis must be approved before the candidate is allowed to proceed to Examination. The candidate in Chemistry may be required to pass a searching examination in one of the following branches:—(1) The Chemistry and Chemical Technology of Inorganic Bodies, including Metallurgy; (2) Organic Chemistry; and to show a thorough practical acquaintance with chemical analysis in all its branches, and with the preparation of pure substances.

HERIOT-WATT COLLEGE, EDINBURGH.

Professor.—John Gibson, Ph.D., F.R.S.E.
Assistant Professor.—John E. Mackenzie, Ph.D., B.Sc.
Demonstrators.—Andrew F. King and James B. Shand.

The Session begins October 9th, 1894.

The curriculum of this College comprises both Day and Evening Classes, each department providing the higher general and technical education.

The Lecture Course to day students in Chemistry is mainly devoted to Inorganic Chemistry. In the Laboratory course each student is required to prepare and study the properties of the principal elementary and compound gases; to perform the more important experiments shown by the Professor in the Lecture Room; to make himself thoroughly acquainted with the preparation and purification of a number of salts. After a careful study of the reactions of the principal metals and acids, he passes on to a full course of systematic qualitative analysis, and may then, if attending a second year, take up an extensive course of quantitative analysis (gravimetric, volumetric, and electrolytic), ultimately making a speciality of any branch of the subject which may be most necessary for his future work. Great attention has been paid to the thorough equipment of the Advanced Laboratories, and special facilities are given to advanced students who may wish to engage in any class of Research (Inorganic or Organic) whether of a purely chemical or of a technical nature.

The teaching in the Evening Classes is based on the Syllabus of the Science and Art Department, and includes Elementary, Advanced, and Honours Courses in Theoretical and Practical Inorganic and Organic Chemistry.

GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.

The main objects of this College are to afford a suitable education to those who wish to qualify themselves for following any industrial profession or trade, and to train teachers for technical schools. It was founded by an Order in Council, dated 26th November, 1886, according to a scheme framed by the Commissioners appointed under the provisions of the Educational Endowments (Scotland) Act, whereby Anderson's College, the Young Chair of Technical Chemistry in connection with Anderson's College, the College of Science and Arts, Allan's Glen's Institution, and the Atkinson Institution were placed under the management of one governing body.

The Diploma of the College is awarded to Day Students who have attended prescribed courses of instruction and passed the necessary examinations. The ordinary courses extend over three years, but arrangements are made for advanced students continuing their studies in special departments.

Complete courses of instruction in Metallurgy and Mining will be given in both Day and Evening Classes.

Copies of the Calendar for 1893-94 may be had from Mr. John Young, B.Sc., the Secretary, 38, Bath Street, Glasgow, price by post, 1s. 4d.

UNIVERSITY OF ST. ANDREWS.

UNITED COLLEGE OF ST. LEONARD AND ST. SALVATOR.

Professor of Chemistry. — T. Purdie, B.Sc., Ph.D., Assoc. R.S.M.

The Session begins on October 10th. A Competitive Examination, open to intending Students of Arts or Science, for about forty Entrance Bursaries, ranging in value from £40 to £10 each per annum, will be held in the beginning of October. Eight of these Bursaries, ranging in value from £30 to £15, are restricted to women, preference being given to those students who intend to proceed to Medicine. Two Degrees in Science are conferred by the University of St. Andrews, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.), and Chemistry is also included in the curriculum for the M.A. Degree; the regulations will be found in the "University Calendar."

Lecture Courses.

Two distinct Courses of Lectures are given, each comprising at least one hundred meetings of the class.

First Year's Course.—This Class meets at 11 o'clock on five days in the week. The introductory lectures treat of the Nature of Chemical Action, the Classification of Substances into Elements and Compounds, the Phenomena of Oxidation, and the Composition of Air and Water. The Laws of Chemical Combination and the Atomic Theory are next discussed, after which the more commonly occurring elements and inorganic compounds are described systematically.

The chemistry of manufactures is referred to only cursorily; special attention, on the other hand, is given to those parts of the science which are of general educational value, and as much of the theory of chemistry is introduced as is compatible with elementary treatment. The Lectures are supplemented by a short Course of Laboratory Practice, intended to illustrate the principles of the science.

These courses of instruction are intended to meet the requirements of the Arts' Curriculum; also of candidates for the First B.Sc. Examination, and of students of medicine, so far as Theoretical Chemistry is concerned.

Second Year's Course.—The first part of the Course is devoted to Organic Chemistry, and the second part treats of the General Principles and Theory of Chemistry, and of more advanced Inorganic Chemistry, the instruction in general being such as is required for the Second B.Sc. Examination.

Certificates are awarded on the results of examinations, and the "Forrester Prize" of about £13 is awarded to the best Student of the year.

Fee for the Session, for each Course, £3 3s.

Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4

p.m., except on Saturdays, when it is closed at 1 p.m. The work pursued in the Laboratory comprises:—(1) The performance of experiments illustrative of the Principles of Inorganic and Organic Chemistry; (2) Qualitative and Quantitative Analysis; (3) Original Investigation. Each student pursues an independent course of study under the supervision of the Professor or Demonstrator, the nature of the work varying with the proficiency of the student and the particular object he may have in view. Suitable courses of instruction in Practical Chemistry are provided for candidates for the First and Second B.Sc. Examinations, and for Students of Medicine.

The fees for Practical Chemistry vary according to the number of hours taken weekly. A certain number of working places in the Laboratory will be available without fee for students who are capable of undertaking original investigation.

QUEEN'S COLLEGE, BELFAST.

Professor.—E. A. Letts, Ph.D., D.Sc., F.R.S.E., &c.

I.—*Chemistry.*—The lectures are delivered at 3 p.m., on the first five days of each week until the beginning of April, and on three days of each week after May 1st, at 2 p.m. The course is divided into three parts:—(1) Chemical Philosophy; (2) Inorganic Chemistry; (3) Organic Chemistry.

II.—*Advanced and Organic Chemistry.*—Lectures on these subjects are given during the first or second terms, or from May 1st until the middle of July, as may suit the convenience of the class. Fee, £1.

III.—*Practical Chemistry.*—In this course the Students are instructed in the general methods of conducting Chemical Analyses. Fee, £3.

IV.—*Laboratory Pupils.*—The Chemical Laboratory is open from November until the end of March, and from May 1st until the third week of July, on the first five days of the week, from 10 a.m. until 4 p.m. Students are admitted as working pupils on payment of a fee of £5 for the first period, or of £3 10s. for the second period (or for a single term).

The Government have just completed new Chemical Laboratories, fitted with all the most recent arrangements, to accommodate 120 students.

Scholarships.—In addition to various Scholarships awarded in the Faculties of Arts and Medicine in which Chemistry forms a part of the examination, there are other valuable Scholarships awarded specially in connection with the schools of Chemistry and Physics.

QUEEN'S COLLEGE, CORK.

Professor.—Augustus E. Dixon, M.D.

Assistant.—D. J. O'Mahony, F.C.S.

The College Session begins on October 16th, 1894, and ends on June 8th, 1895. The classes are open to male and female students.

Systematic Chemistry.—(1) General course of Inorganic Chemistry, Elementary Organic Chemistry, and Chemical Philosophy.—Fee for each Sessional Course, £2. Each subsequent Course, £1. (2) Advanced Organic Chemistry, and Chemical Philosophy.

Practical Chemistry.—(1) The General Course of Practical Chemistry, consisting of about forty Lectures of two hours each, begins on January 7th, 1895.—Fee for each Sessional Course, £3. (2) A Course for Pharmaceutical Students. (3) Special Courses.

The Chemical Laboratory is open daily from 10 to 4 o'clock (except during class hours and on Saturdays) under the Superintendence of the Professor, to Students entering for special courses of qualitative and quantitative analysis; organic chemistry; or for the purpose of original investigation.

QUEEN'S COLLEGE, GALWAY.

Professor.—Alfred Senier, Ph.D., M.D., F.I.C.

The College Session is divided into three terms. The First Term extends from October 17 to December 23, the Second Term from January 8 to March 17, and the Third Term from March 31 to June 12.

The study of Chemistry is pursued throughout the Session by means of experimental lectures and by practice in the laboratory, where each student works independently. Attention is also directed to those technical applications of the science which the wants of the students or the special needs of the West of Ireland appear to demand.

Theory of Chemistry.—(1) A General Course of about seventy lectures is given in the First and Second Terms, embracing inorganic and organic chemistry, the non-metallic elements, the atomic theory, the metals, and the synthesis and properties of the more important fatty and aromatic compounds and their probable constitution. (2) A Special Honour Course of about twenty lectures is given in the Third Term. This course is devoted chiefly to organic synthesis, and includes a review of some of the latest researches.

Experimental Work.—(1) A General Course of about forty lessons of two hours each is given in the laboratory in the First and Second Terms, embracing the elements of qualitative analysis and the chemical examination of urine. (2) Special Courses of experiments in volumetric and gravimetric analysis, in inorganic and organic preparations, and in the applications of chemistry to medicine and the arts are arranged to meet the requirements of the students.

For prospectuses and further particulars apply to the Registrar.

ROYAL COLLEGE OF SCIENCE FOR IRELAND, STEPHEN'S GREEN, DUBLIN.

(SCIENCE AND ART DEPARTMENT).

Professor of Chemistry.—W. N. Hartley, F.R.S.

Assistant Chemist.—Hugh Ramage, F.I.C., Associate of the Royal College of Science, Dublin.

Demonstrator of Chemistry and Assaying.—E. V. Clark, Associate of the Royal College of Science, London.

The Session commences on Monday, October 1st, 1894, and ends on June 21st, 1895.

The Royal College of Science for Ireland supplies, as far as practicable, a complete course of instruction in Science applicable to the Industrial Arts, and is intended also to aid in the instruction of teachers for the local Schools of Science.

Diplomas are awarded in the Faculties of Mining, Engineering, and Manufactures. The Diploma of Associate of the Royal College of Science in the Faculty of Manufactures is recognised by the Council of the Institute of Chemistry of Great Britain and Ireland as qualifying candidates for admission to the practical examinations of the Institute.

The instruction in Chemical Science includes (1) General Chemistry; (2) Advanced Chemistry, including Chemical Manufactures and Metallurgy; (3) Analytical and Experimental Chemistry; (4) Instructions in Chemical Research.

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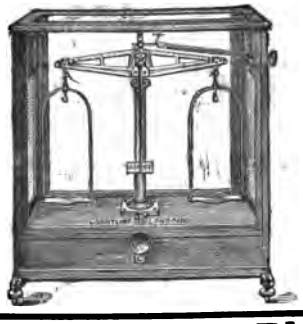

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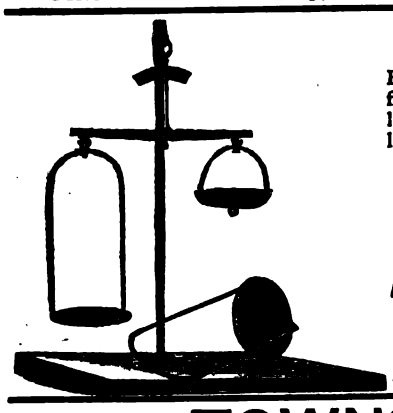

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THE CHEMICAL NEWS.

Vol. LXX., No. 1817.

ON SCHULLER'S YELLOW MODIFICATION OF ARSENIC.*

By HERBERT McLEOD, F.R.S.

An apology seems to be due to the Section for bringing before it a discovery made nearly twelve years ago; but as it seems to be little known, in this country at least, I take the liberty of describing a modification of arsenic discovered in 1882 by Schuller.

Being desirous of obtaining a good specimen of arsenic for lecture illustration, I heated a mixture of commercial arsenic and charcoal in a piece of combustion tube, in a current of carbonic anhydride. The portion of the tube containing the sublimate was sealed off by the blowpipe from that holding the residue; it was then connected with the Sprengel and exhausted, and the arsenic was re-sublimed *in vacuo*. During the operation a small quantity of a yellow sublimate was formed, and, as this was supposed to be arsenious sulphide, the arsenic was mixed with potassic cyanide, and again sublimed. On heating the purified substance *in vacuo* the yellow body was again produced, and rapidly changed to a black deposit.

Some arsenic was obtained by heating arseniuretted hydrogen, free from sulphuretted hydrogen, in a combustion tube; when this specimen was heated *in vacuo* some of the yellow deposit was formed. The end of the tube containing the arsenic was heated in the vapour of boiling mercury for eight hours, when most of the arsenic was volatilised: when the sublimate at the upper end of the tube which presumably contained the more volatile portions, if the substance was not homogeneous, was heated, the yellow deposit was produced, and the portion that remained at the bottom of the tube exhibited the same phenomenon when similarly heated.

The whole of the arsenic in the tube was volatilised in about an hour when heated in the vapour of boiling sulphur.

The yellow substance is extremely unstable, being transformed spontaneously into ordinary arsenic in about one minute: the change commences at the warmer part of the deposit, and gradually passes to the cooler portions; possibly the yellow body might be preserved for a longer time if it were volatilised in a tube with a central tube cooled by a current of cold water.

No mention of the yellow modification occurs in any text-book to which I have referred, and it seemed remarkable that the phenomenon had not been previously observed, especially as it may be obtained by heating arsenic in a tube containing carbonic anhydride at about the ordinary pressure, and it must have been seen by many chemists who have reduced arsenical compounds in a stream of carbonic anhydride.

I should have brought this observation to the notice of the Section under the title of "An apparently new Allotropic Modification of Arsenic," if I had not been referred to a paper by Retgers (*Zeitschr. fur Anorg. Chemie*, vi., 317—320), in which he mentions the work of Schuller. This modification of arsenic was first described in a paper on "Distillation *in vacuo*," by Schuller, read before the Hungarian Academy of Science, on November 13th, 1882, and printed in the *Annalen der Physik und Chemie*, 1883, N.F., xviii., p. 317, in which the volatilisation of a large number of substances is mentioned, and it has thus escaped the attention it deserved.

* A Paper read before the British Association, Oxford Meeting Section B.

THE EFFECTS OF PRESSURE UPON THE BREAKING-STRAIN AND CLEAVAGE OF PAPER AND PAPER-PULP.

By CLAYTON BEADLE.

The amount and direction of the pressures exerted upon a web of paper when in its half-finished state directly influences the strength of the paper produced. A satisfactory explanation has been found for the cleavage of certain rocks, and I venture to think that the same causes appear to explain the peculiarities of paper in this respect.

Slaty cleavage is in no sense due to the stratification of the rock during its formation, as the planes of cleavage stand in most cases at right angles to the bedding. Geologists are satisfied that it is distinct from crystalline cleavage. Mr. Sorby, the geologist, found that plates of mica are a constituent of slate rock. He found by applying pressure to a mass containing scales of oxide of iron and sand, that the scales tended to set themselves at right-angles to the direction of the pressure, and attributes slaty cleavage to the formation of the rock under great pressure, tending to set the plates of mica at right-angles to the pressure exerted, and to allow of cleavage in the direction of these plates.

In the process of the manufacture of paper, the pulp as it passes on to the endless wire of the machine consists of "ultimate" vegetable fibres, such as cotton, linen, and wood, suspended in a large volume of water. The specific gravity of these fibres is about 1·5. It must be remembered that they differ from plates of mica in that they present no plane surfaces.

As the mass passes on to the wire it receives a lateral shake which tends to set the fibres at right-angles to the force exerted by the shake. This might be at right angles to the surface of the liquid or in a plane parallel to it. The latter direction appears to be determined partly by the force of gravity, which first of all carries the fibres through the medium in which they are suspended and causes them to press one on the other. The fibres are retained by the wire gauze, but the watery medium filters through. Water unable to filter through is removed by—(1) the suction boxes, and (2) the press rolls. The water, then, is removed by forces acting at right angles to the surface of the web; so that we have two sets of forces. One exerted in a direction at right-angles, that in which the web is travelling, but in a plane parallel to the surface of the web; and the second in a vertical direction. These two forces acting together cause the fibres to lie in the direction in which the web is travelling.

From a comparison of the breaking-strain of machine-made papers, across the web and in the direction of the web, it has been found that across the web the paper is from 20 per cent to 40 per cent stronger than in the direction of the web, which is undoubtedly due to the fibres lying more in the latter direction.

With hand-made papers this is not the case, as the shake is produced in two directions, at right-angles to each other, and in a longitudinal plane; the fibres, therefore, have no tendency to lie in any one longitudinal direction. The fibres are more thoroughly interlaced, and the strength of the paper, generally speaking, uniform, and superior to that of machine-made papers.

When a paper is thick, and the water is not thoroughly removed on the wire, more work is thrown on the press rolls. This gives the paper a greater tendency to laminate and to admit of cleavage. The same effect is produced also with hand-made papers by pressure applied after placing the sheets between felts to remove the surplus moisture. For this reason I believe some papers admit of being split with a fair amount of readiness, each sheet forming two of half the original thickness.

It is found that when paper-pulp is subjected to

hydraulic pressure for the removal of water, and the cakes so produced allowed to dry, that the mass may be readily broken asunder in a plane at right-angles to the direction in which the pressure has been applied. These blocks often have every appearance of stratification, and can be made to separate in distinct and well-defined layers.

Paper-pulp that has been allowed to dry without the application of pressure does not exhibit this property.

THE APPEARANCE OF CHROMATES IN PAPER AND PAPER-PULPS.

By CLAYTON BEADLE.

The production of a bright yellow deposit when bleaching the half-stuff obtained from a certain class of rags in the beater was brought to my notice about three years ago. On examination this deposit was found to be lead chromate; it was found in the stuff only where certain lodgments took place under the cover of the beater roll. The rags were mostly "coloured pieces," and the ash from the same, both before and after boiling, was found to contain chromium in large quantity. The bleached half-stuff contained only a fraction of the chromium found in the unbleached rags. The water drained from the stuff contained chromium as chromic acid, and traces of chromium were detected in the back water from the machine and in the paper where these rags had been used.

On placing these chrome-mordanted rags in a dilute solution of "bleach," whether before or after boiling, it was found that even in the cold a considerable quantity of the chromium salts had been oxidised to chromic acid and gone into solution.

The peculiar appearance of lead chromate in the stuff in certain parts of the beater seemed more difficult to explain. The beater was lead lined, and the cover of the beater roll was made of solid zinc. The latter was separated from the lead lining in places only with a piece of felt which was continually kept wet by contact with the solution. On removal of the cover, the strip of felt was found to be deeply and evenly dyed with lead chromate.

The following experiments were tried, which proved conclusively to us that the deposition of lead chromate is due to galvanic action:—

A strip of lead was placed in contact with a piece of felt immersed in the solution for twenty-four hours. No lead chromate was formed.

A strip of lead and a strip of zinc were placed between a felt, without allowing contact of the metals, and immersed in the solution twenty-four hours. No lead chromate was formed.

The latter experiment was repeated, but allowing contact of the two metals. In twenty minutes the felt was stained yellow, and in two hours a considerable quantity of lead chromate was deposited. On examination of the lodgments of the stuff it was found that the yellow colour was produced only where the lumps were in contact with the two metals in such a manner as to complete a circuit.

Australasian Association for the Advancement of Science.—It is now decided that this Association will hold its next annual meeting on January 11th, 1895, at Brisbane.

Inverting Effects of Glycerin.—Ed. Donath.—The author emphasises the fact that hitherto we possess no satisfactory theory of the hydrolytic scissions of the different organic substances. He has therefore studied the inversion of certain sugars of glycerin. Anhydrous glycerin or such as contains but little water has a relatively feeble inverting action, whilst it increases on dilution with 10 per cent, and still more with 20 per cent of water.—*Journ. f. Prakt. Chem.*, Part 12, 1894.

THE ESTIMATION OF POTASH IN MANURES.

By VINCENT EDWARDS, F.C.S.

As the estimation of potash in manures by the methods usually found in text-books is troublesome and tedious, being wholly unsuitable when rapid work is required, the following slight modification may be of use to chemists who have many of the determinations to perform and whose time is limited.

I take about 1 grm. of the well-mixed sample, and, if it contains much organic matter, first ignite gently in a platinum dish. When cold, the ash is boiled with water for a few minutes in a small beaker, a drop or so of hydrochloric acid being added if difficult to dissolve; on cooling I add slight excess of strong ammonia and a little solution of ammonium oxalate; then filter through a Swedish paper into a platinum dish, and add dilute sulphuric acid to the filtrate till acid to test-paper; then evaporate to dryness on the water-bath, and ignite very carefully; dissolve in hot water, with the addition of a few c.c. of HCl, and wash into a small porcelain basin; add excess of solution of platinum chloride, and evaporate if possible below boiling to a moist paste. On cooling, add about 20 c.c. of water containing a few drops of platinum chloride solution, and carefully decant off the liquid into another porcelain basin. By a little careful manipulation all the double salt will be left in No. 1 basin. Repeat the process three times with alcohol, and once with ether; then put the basin in the water-oven till quite dry, brush out the double salt into a watch-glass, and weigh when cold. This dispenses with the usual weighed filter-paper; and if carefully done no loss need occur, and crystals of the double salt going into No. 2 basin can be washed and weighed along with the contents of No. 1.

Lawes' Works, Barking,
September 1, 1894.

NOTES ON WATER ANALYSIS.

By C. A. SEYLER, B.Sc.

(Concluded from p. 114).

II. *Carbonic Acid (continued).*

The presence of *free* carbonic acid is an almost constant characteristic of ground water. The amount varies considerably, and may reach about 13 m.grms. per 100 c.c. It is distinctly correlated to the amount of dissolved oxygen, varying in the opposite direction, since most causes which tend to impart free CO_2 also tend to remove free oxygen, and *vice versa*. Deep water would seem, however, to be relatively poorer in oxygen than shallow. On an average, in nineteen waters described as wells, was found—Free CO_2, 3·3 m.grms. per 100 c.c.; dissolved oxygen, 4 c.c. per litre: while in fifteen spring waters, free CO_2, 2·7 m.grms.; dissolved oxygen, 5·9 c.c. per litre.

The source of the free CO_2 in ground water is, no doubt, that in the ground air, and the amount of this (according to Pettenkofer and others) follows almost exactly the seasonal variation in the amount of nitrification. It also increases with the depth and decreases with the porosity of the soil, both important factors in the efficiency of natural filtration. The quantity of free CO_2 in ground water does not appear, however, to be related to the absolute amount of nitrification; for instance, it is very high in some well waters containing ferrous salts, in which nitrification is characteristically absent, although ammonia may be present.

Owing to want of precise information as to the history of the samples examined, few general conclusions can be at present drawn, but it is probable that the application of the above methods to the systematic study of ground

water, and of the effects of percolation (on the lines of Warington's paper on Well Water, *Journ. Chem. Soc.*, 1887), would yield valuable results.

When a ground water is subsequently exposed to the air it may rapidly lose its free CO_2, and even become alkaline to phenolphthalein. I have examined seven such cases. They are generally waters containing magnesic carbonate, and evidence the fact of their exposure by saturation with dissolved oxygen. A typical case is that of a well water suspected to be influenced by the tide, and containing an enormous amount of chlorine. The same well in the morning contained free CO_2, 1·91 m.grms. per 100 c.c., combined 13·4; and in the evening had become alkaline to phenolphthalein, now containing free CO_2 none, half-bound 7·8, combined 10·0. The first sample was found to lose all its free CO_2, and become alkaline upon standing in a beaker for twenty-four hours.

There are two other respects in which the estimation of the free and combined CO_2 is of interest, one the reaction of a water, and the other its action on lead. The reaction is generally taken by means of the so-called neutral litmus-paper. If any considerable amount of combined CO_2 be present, the reaction will generally be returned as very slightly alkaline. I have, however, found that waters containing both free and combined CO_2 may be distinctly *amphoteric*,—that is, turn red paper blue, and blue paper red, and within very wide limits. The following are examples of waters possessing this property:—

	Free CO_2.	Combined CO_2.
1.	1·98	13·42
2.	3·85	11·22
3.	7·70	2·31
4.	5·72	3·63
5.	2·09	3·08
6.	10·20	2·42

The amphotery to litmus is simply the result of competition for the base between the free carbonic acid and the red litmus, which is itself a weak acid having blue salts. When the red paper is placed in a solution containing carbonates and free carbonic acid, it seizes a portion of the base until equilibrium is established. If the blue paper be placed in the solution, the free carbonic acid robs it of a part of the base, and liberates red litmus until the same condition of equilibrium is reached. Thus the expressions "alkaline," "acid," or "neutral," to litmus have no definite meaning unless the precise condition of the litmus-paper is specified. The "neutral" paper contains both red and blue litmus, not necessarily in equivalent amount, but simply so that the red and blue tints are approximately equal in intensity. Testing the reaction with litmus-paper is thus much better replaced by the estimation of the free and combined CO_2.

Action on Lead.—This is still largely a mysterious subject, but there is no doubt that the relative amounts of free and combined CO_2 are important factors in determining the lead-dissolving power of a water. In all waters I have examined which had the property, free CO_2 has been present in amount equal to or larger than the combined, even when the latter is as much as 2·5 m.grms. per 100 c.c. Such a water may be distinctly alkaline to red litmus-paper. In testing the action on lead it is essential to conduct the experiment in a closed vessel, as well as in open beakers, to prevent loss of free CO_2, as the results will be sometimes found positive in the former and negative in the latter case. In several cases of strong solvent action free H_2SO_4 was found to be present.

To conclude, there is much in the estimation of the free and combined carbonic acid to render their determination of value to the analyst, and the expenditure of time, labour, and material involved is insignificant. It is much to be desired that the above method should be better known and systematically used in this country, especially by those who have opportunity for study of waters of known history.

(To be continued).

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING AUGUST 31ST, 1894.

By WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, September 10th, 1894.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 178 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from August 1st to August 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 178 samples examined, all were found to be clear, bright, and well filtered.

The rainfall over the Thames Valley during the month of August has shown an excess of nearly a quarter of an inch over the 25 years' average; the recorded fall at Oxford being 2·48 inches, and the mean for 25 years 2·24 inches for the same month. The excess of rainfall over the averages for the months of June, July, and August now amounts to 1·71 inch.

The quality of the waters during August has kept up to the high average of the summer months; the analytical results showing very little difference. The slight variations from the June and July tables in almost all cases being accounted for by the increased rainfall and consequent dilution.

The estimation of the absolute amounts of the carbon and nitrogen (as constituents of the organic matter) present in the various samples is effected by organic combustion of the solid residue which results from the evaporation of a known quantity of the water. The whole amount in each case is so small that the figures may be stated as expressing units and fractions of a unit in a million parts by weight of the water.

In the experimental conduct of such refined analyses, each analyst has a personal equation which represents the correction which ought to be made in his results, so that they may express absolute accuracy. It is important, however, that each analyst should continue to follow his own mode of working, and in the event of any change in the conduct of the operations to announce the fact and the difference brought about by the modification of the process. No substantial change has been made in the process of organic combustion since the beginning of these Reports. The inference is, therefore, that any small correction in the analytical figures that may be necessary must be applied uniformly to the whole of the previous results. Such correction could in no way, however, modify the inferences to be drawn from the results.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.
JAMES DEWAR.

ON THE

ANALYTICAL PROPERTIES OF IRON PHOSPHIDE AND PHOSPHATE.*

By L. M. DENNIS and B. S. CUSHMANN.

In the year 1886, Cheever, in an article in the *Transactions of the American Institute of Mining Engineers* (xv., 448), sought to explain the variation in effect of a definite amount of phosphorus upon the properties of iron and steel by assuming that the phosphorus exists in the metal in two conditions: viz., as phosphide, which is harmful, and as phosphate, which is harmless, or comparatively so. To demonstrate this he used the following method:—

A weighed sample of iron is treated in the cold with a solution of the double chloride of copper and ammonium until the iron is all dissolved, then filtered without washing. The residue of copper, carbon, phosphorus, &c., is next digested at 50° C. for two hours with 100 c.c. of a saturated solution of ammonium oxalate, then filtered and washed; the filtrate contains the phosphate of iron, the residue the phosphide.

Later, in the same article, he shortens the method as follows:—

The copper, carbon, phosphorus, &c., residue is shaken in a flask for five minutes with 75 c.c. of a cold 1 per cent solution of hydrochloric acid (2 c.c. strong hydrochloric acid to 100 c.c. water—free from chlorine), then filtered and washed with water, the filtrate made strongly acid with nitric acid, and evaporated nearly to dryness, and the phosphorus precipitated by molybdate solution.

In a second paper in the same journal (xvi., 269), Cheever gives results obtained by another method, he here volatilising the iron as chloride by chlorine, "and analysing the residue for phosphorus, which, if present, must be in the form of phosphoric acid; for the iron phosphide would be volatilised."

At that time doubt was cast upon the accuracy of Cheever's work because of the uncertainty as to the behaviour of phosphide of iron towards the different reagents which he employed. In the hope of removing some of that uncertainty, the authors entered upon the experimental work detailed below.

Preliminary work upon the phosphides of iron carried out by Mr. Russell Elliott in this laboratory in 1891-92, seemed to show that the different phosphides, of which, according to Freese (*Pogg. Ann.*, cxxxii., 225), there are three, Fe_3P_4, FeP, and Fe_2P, behave quite similarly towards various solvents. For this reason, and also because of the length of time required for the preparation of a pure sample, we prepared and examined only one of the phosphides, selecting that which is formed by treating anhydrous ferrous chloride with phosphine at a red heat.

Ferrous Chloride.—The purest piano-wire obtainable was placed in a combustion tube, which was connected on one side with an apparatus furnishing dry hydrochloric acid gas, and on the other side with a Schiff nitrometer (*Zeit. Anal. Chem.*, vii., 430) filled with strong potassium hydroxide solution. When the air in the tube had been completely displaced by the hydrochloric acid gas, as was shown by the complete absorption of the gas by the caustic potash solution, the combustion-tube was heated to redness. The ferrous chloride produced was partly in the form of glistening light yellow plates, and partly a yellowish amorphous powder. Careful tests showed that it was completely free from ferric chloride.

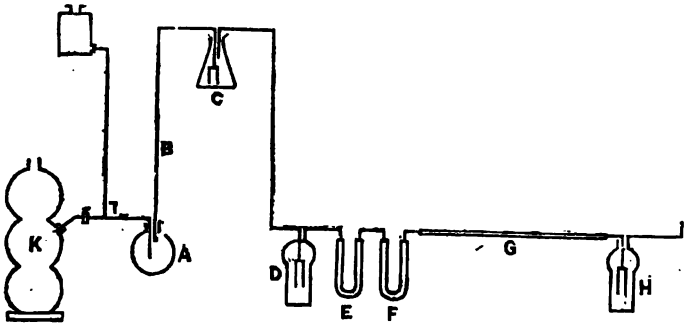
Phosphine.—The phosphine was generated by the action of a solution of potassium hydroxide upon phosphorus. The form of apparatus finally adopted has given such satisfactory results that a brief description of it may not be out of place. It consists of:—

1. The 500 c.c. distilling flask, A, in which the phosphine is generated.
2. The upright tube, B, which serves as a condenser, and which is widened after entering the cooling flask, C, to prevent its becoming clogged by the condensation of the phosphorus.
3. The cooling flask, C, which is surrounded with ice-water.
4. The wash-bottle, D.
5. The two U-tubes, E and F, filled with calcium chloride for drying the gas.
6. The combustion-tube, G.
7. The wash-bottle, H, which prevents the air from diffusing back into the combustion-tube.
8. A Kipp apparatus, K, for generating hydrogen.
9. The T-tube, T, through which water could be driven into A from the reservoir above in order to stop the generation of the phosphine by diluting the caustic potash solution.

The most uniform evolution of phosphine was obtained by using a 1 : 1 solution of potassium hydroxide, a stronger solution causing a more rapid generation of the gas than was desirable. Although the phosphine resulting from the use of this moderately concentrated potash was not as pure as that obtained with a very concentrated solution (A. W. Hofmann, *Ber. d. Chem. Ges.*, 1871, 200), yet the phosphide obtained was probably not influenced to any great extent by the small amounts of hydrogen given off early in the phosphine evolution. The hydrogen would reduce some of the ferrous chloride to metallic iron, but if we accept the statement of Freese (*Pogg. Ann.*, cxxxii., 225), the product is the same whether phosphine acts upon anhydrous ferrous chloride or upon metallic iron. To avoid, however, the production of any unnecessary large amount of hydrogen the contents of the generating flask was at no time heated to boiling, this precaution serving to lessen the amount of hydrogen arising from the secondary reaction between the potassium hydroxide and potassium hypophosphite:—

$$KH_2PO_2 + 2KOH = K_3PO_4 + 2H_2.$$

It was thought that the hydrogen thus set free might reduce the phosphide after the latter had formed, but later experiments with the pure phosphide showed that it was not reduced when highly heated in a current of hydrogen. The solution of potassium hydroxide should be cooled before being poured upon the phosphorus in the



* From the *Journal of the American Chemical Society*, xvi., No. 7.

flask, in order to avoid the immediate generation of any phosphine, as that would cause an explosion upon coming in contact with the air in the flask. As soon as all connections had been made, hydrogen from the Kipp generator was run through the apparatus until all air had been expelled. The sand-bath under the generating flask was then gently heated until the phosphine began to come off somewhat rapidly. The hydrogen was then shut off and the flame removed, the latter being replaced only when the solution of the gas had nearly ceased. This procedure greatly lengthened the duration of the current of phosphine.

When nearly all of the hydrogen had been driven from the apparatus the phosphine burst into flame at the end of the outlet tube. The combustion-tube was then heated. As soon as the hydrochloric acid gas, formed by the action of the phosphine upon the ferrous chlorine, began to come off, the flame at the outlet tube ceased to burn. The ferrous chloride gradually darkened, and after half an hour, when the reaction was completed, it had assumed a dark bluish grey colour.

Upon breaking the tube there was found a brittle porous substance which rarely showed any crystalline structure. It was powdered in an agate mortar, then digested with hot hydrochloric acid (1 : 12) until it was not at all attracted by the magnet, and was finally dried over sulphuric acid in an atmosphere of carbon dioxide.

Analysis of the Phosphide.—Stöckmann (*Zeit. Anal. Chem.*, xvi., 175) states that he always obtained too low results for phosphorus when aqua regia was used as a solvent for spiegeleisen. He also tested the gases which were given off when the sample was dissolved, by passing them through an oxidising medium, and in each case was able to detect phosphorus in them. For this reason we first tried other solvents, but although the phosphide was quite strongly attacked by nitric acid and by hydrochloric acid, and especially by nitric acid to which potassium chlorate was gradually added in small amounts, complete solution was in no case effected even by several hours treatment.

Portions of the phosphide were then treated with aqua regia in a small flask to which a return-flow condenser was attached. After passing through the condenser the escaping gases were passed through a Mitscherlich bulb containing a solution of potassium hydroxide which had previously been saturated by chlorine. After the phosphide had been completely dissolved, the potassium hydroxide solution was acidified with nitric acid, and was repeatedly evaporated with nitric acid until all chlorine had been expelled. Ammonium molybdate was then added, but no trace of a precipitate resulted. Aqua regia was, therefore, adopted as the solvent for the sulphide.

The following method of analysis was first tried :—

About 0·1 grm. of the phosphide was dissolved in aqua regia (1 part of nitric acid to 3 parts of hydrochloric acid), and the solution, after being diluted, was precipitated by ammonium hydroxide. An excess of ammonium sulphide was then added to break down the ferric phosphate, and the solution was kept at 70° C. for fifteen hours. The ferrous sulphide was then filtered off, dissolved in dilute hydrochloric acid, and the iron then oxidised by bromine water. Upon precipitating this solution with ammonium hydroxide and weighing the iron as ferric oxide, too high results were obtained since the precipitate was found to contain phosphoric acid.

The method finally adopted for the analysis of the phosphide was as follows :—

The sample was dissolved in aqua regia, the solution repeatedly evaporated with nitric acid, and the phosphoric acid determined by the molybdate-magnesia method. To determine the iron in the filtrate from the ammonium phosphomolybdate precipitate, the method of W. H. Krug (*Journ. Anal. Appl. Chem.*, v., 674) was used with satisfactory results. The iron was precipitated in the cold with ammonium hydroxide, and the ferric hydroxide, after thorough washing, was dissolved in nitric acid and again precipitated from the cold solution with ammonium hydroxide. After washing until all chlorides had been removed, the iron was weighed as Fe_2O_3.

The results obtained were as follows :—

	Found.	Calculated for	
		Fe_3P_4.	FeP.
Fe	64·21	57·52	64·36
P	35·62	42·48	35·64

The work of other investigators in this field has led us to expect as a product, not FeP, but Fe_3P_4. Yet the constancy of composition shown by separately prepared portions of our product, its completely non-magnetic character, and the agreement of the analysis with the calculated percentages, leave but little doubt as to the purity and identity of the phosphide.

The fact that the true phosphides of iron are *non-magnetic* seems to have been overlooked by recent writers—a circumstance which has probably led Hvoslef, Schneider, Percy, and others to regard a mixture of phosphide of iron and iron (they give it the formula Fe_3P) as a definite phosphide. Howe ("Metallurgy of Steel," p. 55) cites the work of Hvoslef and Percy, and says :—"These facts suggest that iron and phosphorus preferentially combine in this particular ratio." But he does not mention the careful and extended researches of Freese upon this subject, who says (*Pogg. Ann.*, cxxxii., 262) :—"Endlich habe ich versucht, das von Hvoslef beschriebene Phosphoreisen Fe_3P, welches derselbe durch Glühen des Phosphorets FeP unter einer Decke von Borax erhalten haben will, darzustellen, allein bis jetzt vergeblich." After describing some of his own experiments, made according to Hvoslef's method, Freese concludes :—"Hieraus schliesse ich, dass Hvoslef's Phosphoreisen nur ein Gemenge von Eisen mit Phosphoreisen ist, denn stets fand ich bei einem anerkannt reinen Eisenphosphoret den nach längerer Behandlung mit heisser Chlorwasserstoff saüre verbliebenen Rückstand mit dem Phosphoret gleich zusammengesetzt."

Ferric Pyrophosphate.—This salt was chosen as representing perhaps more nearly than any other the condition of the oxidised phosphorus in iron and steel. A sample of the pure ferric pyrophosphate was heated for half an hour over the full Bunsen flame; it retained its yellow colour and was completely soluble in concentrated hydrochloric acid.

Experiments with Solvents.—Before attempting to separate the phosphide of iron from the pyrophosphate in samples of iron or steel, it was necessary to find a solvent which would completely dissolve the pyrophosphate and leave the phosphide unattacked. The reagents tried were solutions of ammonium oxalate, potassium oxalate, ammonium citrate, ammonium citrate, ammonium carbonate, ammonium cupric chloride, and dilute solutions of chromic, sulphuric, nitric, and hydrochloric acids; both rapid boiling and long digestion at 100° C. were employed. Clear solutions of the pyrophosphate were obtained only with ammonium oxalate, ammonium citrate, and hydrochloric acid. Portions of 50 m.grms. of the pyrophosphate were then digested on a hot plate with 100 c.c. of each of these three solvents. Complete solution resulted—

With hydrochloric acid (1 : 1)	in 2 minutes.
,, ammonium oxalate (concentrated)	,, 45 ,,
,, ,, citrate (sp. gr. 1·09) ..	,, 90 ,,

On diluting the ammonium oxalate solution with water, a white precipitate resulted, and as this could be dissolved only by adding hydrochloric acid and boiling, the use of ammonium oxalate was abandoned.

One hundred m.grm. portions of the phosphide were then treated with hydrochloric acid and ammonium citrate under the same conditions as were required for the complete solution of the pyrophosphate. The residues were collected on counterpoised filters, dried, and weighed.

It was found that the phosphide which had been digested with hydrochloric acid had lost about 4 per cent of its weight. The filtrate from this portion, after the hydrochloric acid had been expelled by evaporation with nitric acid, gave strong tests for both iron and phosphorus. The sample of phosphide which had been digested with ammonium citrate showed no appreciable loss of weight, and hence a solution of this reagent, of a sp. gr. of 1·09, was used in the following experiments upon the separation of the pyrophosphate of iron, and phosphide of iron, in samples of iron and steel.

Before trying the ammonium citrate solution a preliminary experiment was made to ascertain the nature of the action of hydrochloric acid (1 : 1) upon the phosphorus in iron. A sample of pig iron, containing 0·205 per cent total phosphorus, was treated with the acid until all action had ceased. The solution was filtered, the filtrate evaporated with nitric acid, and the phosphorus determined by the molybdate-magnesia method. Two determinations gave 0·153 and 0·154 per cent phosphorus. The determination of the phosphorus in the unattacked residue showed that only 0·008 per cent remained behind, from which it follows that over 20 per cent of the phosphorus present escaped in gaseous form during the solution of the iron.

The ammonium-citrate separation was then tried on two samples of steel, to ascertain whether the method would give agreeing results. The sample should be as finely divided as possible, and for this reason filings were used in the following determinations:—

Five grms. of "Open Hearth" steel were digested on a hot plate (100°), with ammonium citrate solution, for an hour and a half. The solution was then filtered through asbestos. The residue was thoroughly washed with water, dissolved in nitric acid (1·20 sp. gr.), and the phosphorus determined by the molybdate-magnesia method.

Total phosphorus in the sample was 0·044 per cent.

Phosphorus in the residue, after treatment with ammonium citrate, 0·033 and 0·032 per cent.

A sample of Bessemer steel, containing 0·107 per cent total phosphorus, gave by the same method 0·046 and 0·053 per cent of phosphorus in the residue.

No further analyses of iron or steel samples were made, for our object in taking up the work was not the investigation of the condition of phosphorus in samples of commercial products, but was merely to attempt to devise a method to separate phosphide of iron from pyrophosphate.

The chlorine method employed by Cheever was also tried on the phosphide and pyrophosphate.

Eighty m.grms. of the phosphide were heated in a current of dry chlorine. As the temperature rose, sparks shot out from the surface of the phosphide. At a low red heat a glow ran through the substance, which then melted and volatilised completely in a few minutes.

A sample of the ferric pyrophosphate was then heated for half an hour in a current of chlorine at the highest temperature obtainable by the use of a combustion furnace, but no loss in weight resulted.

A mixture of 0·0435 grm. of the pyrophosphate, with 0·0292 grm. of the phosphide, was then heated in chlorine in the same manner. The residue in the boat weighed only 0·0231 grm. As this seemed to indicate that in the volatilisation the phosphide exerts some reducing action on the pyrophosphate, causing a volatilisation of some of the constituents of the latter compound, another experiment was tried with a mixture containing a slightly higher per cent of phosphide, to see whether there would be a correspondingly greater loss in the pyrophosphate.

0·0561 grm. of the pyrophosphate, and 0·0472 grm. of the phosphide, treated with chlorine, gave a residue weighing 0·0193 grm., a result which seems to sustain the above supposition.

RECENT PUBLICATIONS RELATING TO CARBOHYDRATES.*

By W. E. STONE, Purdue University.

(Concluded from p. 119).

Amorphous Carbohydrates.

According to Wortmann, starch is dissolved in plants without the aid of diastase, but a study of the potato shows that its rapid development of vegetating parts at the expense of the starch of the tuber is in direct relation to the amount of diastase in the latter (*a*). Starch seems to undergo complete inversion to dextrose by the action of blood serum (*b*). Mylius has described a compound of starch and iodine of the composition $(C_6H_{10}O_5)_4I$, and two others are now noted, $(C_6H_{10}O_5)_8I$ and $(C_6H_{10}O_5)_{11}$. The three form a series with the following formulæ, $R_{16}I_2$, $R_{16}I_3$, and $R_{16}I_4$ (*c*).

Inulin may be regarded as analogous to starch, and, like starch, is accompanied in nature by a peculiar ferment, inulase. By action of inulase and yeast, inulin is quickly brought into fermentation (*d*). Inulin from *Helianthus tuberosus* may be separated into different forms, which, however, seem to be different aggregation forms of the same material; to these different forms are given the names inulin, pseudo-inulin, and inulenin, which can be distinguished by their different compounds. The properties of inulin may be reviewed as follows:—Granular, loses water slowly over sulphuric acid, sparingly soluble in cold water, wholly soluble in hot water, melts at 178°, specific gravity 1·539. Specific rotation $(\alpha)_D = -39·5$, on inversion is converted into one part dextrose and twelve parts levulose, not coloured by iodine, nor fermentable, nor reducing towards Fehling's solution, and soluble in cold baryta solution, afterwards becoming precipitated (*e*).

Glycogen has been found to possess nearly the same specific rotation as erythro-dextrin, 196·63°, and the reactions of both with iodine are strikingly similar. The same author has prepared glycogen from the blood of different animals and also recognised it in pus. From 100 grms. of different kinds of blood the following amounts of glycogen were obtained:—Swine, 0·661 grm.; sheep, 0·114 grm.; horse, 0·380 grm.; ox, 0·57 grm.; calf, 1·332 grms.; dog, 1·560 grms.; goose, 0·690 grm. It seems to be a constant constituent of blood (*f*).

An investigation of the formation of glycogen from various sugars in the animal organism admits of the conclusion that iso-maltose, levulose, and dextrose form glycogen, directly; mannose at least causes its increase; lactose is of doubtful effect, and that of galactose and the pentoses are as yet not definitely determined (*g*).

Cellulose has been observed in crystallinic forms when microscopic sections of vegetable tissues were treated with Schweizer's reagent and washed with ammonia. The same author recognises two kinds of cellulose, one crystallinic and coloured by the chloriodide of zinc, and the other amorphous and not so coloured (*h*).

Some definite compounds of cellulose and the alkalis have been noted. Such alkali-cellulose forms with carbon disulphide a thiocarbonate of cellulose which presents some curious properties. It absorbs water, swells up strongly, and, on addition of alcohol, a sodium salt of cellulose thiocarbonate is precipitated. From a solution of the latter a hydrated cellulose separates out by coagulation or even on heating. In these different products the proportions of sulphur and sodium remain constant, but the cellulose varies. The authors emphasize the fact that it is an alkali-cellulose which enters into these combinations (*i*).

Physiological.

The chemical and physiological processes occurring in green leaves have been carefully studied with regard to

* *Agricultural Science*, viii., No. 2.

the appearance and disappearance of the carbohydrates in these organs. All leaves examined were found to contain more than enough diastase to dissolve all of the starch ever present. Starch never appears in the leaf cells except when the formation of carbohydrates exceeds their consumption. Most of the assimilation products never take on this form. The starch thus formed is dissolved again by the action of diastase, contrary to Wortmann's theory. The product of this solution is maltose, the same as in malting. Sucrose, dextrose, and levulose, and maltose were the only sugars found in leaves. The authors draw these conclusions:—That sucrose is the first and normal assimilation product in leaves. It accumulates under vigorous action of assimilating processes and at a given stage is elaborated into starch which is a more stable reserve material than sucrose, and is only drawn on when the latter is exhausted. Sucrose is translated as dextrose and levulose; starch is first dissolved and then translocated as maltose (*j*).

The digestibility of the pentosans has been studied by the examination of a number of samples of food and fæces obtained in connection with several different feeding experiments with sheep. Twenty of the best known feeding stuffs were shown to contain from 6 to 16 per cent of pentosans, of which, on the average, only 58·2 per cent are digestible. The conclusion was drawn that these were among the less digestible of the food constituents (*k*).

As regards the digestibility of the pentoses themselves, it has been shown that they are not assimilated by the human organism, being rapidly secreted unchanged in the urine (*l*).

Experiments upon rabbits, however, indicate that arabinose was quickly resorbed. Only one-fifth reappeared in the urine; some arabinose was to be traced in the blood. In the liver was abundance of glycogen but no arabinose (*m*).

Analytical.

The methods of Tollens and his pupils for determining the amount of pentosans in vegetable materials have been summarised after a good deal of patient study of details. The final method approved by them and yielding accurate results consists essentially in distillation of the material with hydrochloric acid of 1·06 specific gravity and precipitation of the furfurol thus obtained as furfurol-hydrazon. The gravimetric method is preferred to the volumetric for determining this furfurol, since it was noted that other products of distillation, such as levulinic acid and acetone, formed soluble compounds with the phenylhydrazin used in titration. The weight of furfurol-hydrazon thus obtained multiplied by 1·13 gives the equivalent in pentoses, and this result multiplied by 0·88 gives the equivalent of pentosans (*n*).

A modification of this method which avoids the difficulty encountered in filtering and drying the furfurol-hydrazon consists in dissolving the precipitate on the filter-paper with alcohol and evaporating the solution in a tared flask at 60°, drying in hydrogen (*o*).

Another method of determining the furfurol involves its precipitation with pyrogallol. The precipitate is filtered and weighed as above, and the weight divided by 1·974 gives the amount of furfurol (*p*).

A proposed convenient method of determining the amount of precipitated cuprous oxide in the titration of glucose consists in bringing the precipitate on a filter and placing the same in a dilute solution of nitric acid in a platinum dish upon which the copper is deposited by electrolysis and weighed (*q*).

Another method for the same determination is to filter on to a double filter-paper, the two papers having been equipoised. After washing, the filters are separated and dried at 65—70° at which temperature the cuprous oxide is said to undergo no change. The precipitate retains 0·3 to 0·4 per cent of organic matter to be deducted from the final weight (*r*).

All of the methods proposed for determining the presence and quantity of grape sugar in urine, some sixteen in number, have been reviewed, and the conclusion arrived at is, that the test with Fehling's solution is after all the most reliable (*s*).

Isomaltose may be determined in the presence of maltose by removing the latter by means of fractional fermentation. A particular kind of yeast (*Satze Hefe*) does not ferment isomaltose (*t*).

The following optical method for the assay of commercial starch is of interest:—5·376 gr. of material (for polariscopes using the normal weight of sucrose as 16·19 gr.) are placed in a 200 c.c. flask of water and boiled forty to fifty minutes, and the flask filled with water; after cooling, add a few drops of ammonia to clear, fill to the graduation mark, and polarise in 400 m.m. tube. The starch thus brought into solution has a specific rotation $(\alpha)_D = 200{\cdot}15°$, and the readings on the polariscope scale give percentages direct. The solution does not reduce Fehling's solution and is stained blue with iodine (*u*).

Multi- or Birotation.

This remarkable phenomenon bids fair to be explained satisfactorily in the near future. Three views are current. Dubrunfaut, Erdmann, and Bechamp hold that optically active bodies exist in crystallinic and amorphous states of different rotatory powers, and that in solution one goes over into the other. Another view is that the simple molecules combine to more complex ones on going into solution or *vice versâ*, the result being indicated by the increase or decrease of rotatory power. The third theory is that a combination with the solvent occurs. In support of this latter view is the observed fact that hydrazons of the sugars are formed much more rapidly with sugars that have just been brought into solution than with those which have been long dissolved and presumably combined with the solvent (*v*).

Another author regards multi-rotation as due to the gradual dissociation of the hydrated compound into the water-free form, which latter then shows the true rotation. For instance, water-free amorphous glucose shows no birotation, but crystallinic glucose does, and it is assumed that the latter on solution forms a hydrate which gradually dissociates, and attains finally a constant rotation (*w*).

Important experimental proof of this also appears in the thermal phenomena noted when sugar is dissolved. When anhydrous dextrose is dissolved, the temporary decrease of temperature is presently followed by a distinct rise, due probably to the formation of a hydrate. If ammonia be added to the solution at the outset, these changes of temperature do not occur nor is any multi-rotation noticed (*x*).

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(*a*) A. Prunst, *Comptes Rendus*, cxv., 751.
(*b*) F. Rohmann, *Berichte d. Chem. Gesell.*, xxv., 3654.
(*c*) G. Rouvier, *Comptes Rendus*, cxvii., 281.
(*d*) E. Bourquelot, *Ibid.*, cxvi., 1143.
(*e*) C. Tanret, *Ibid.*, cxvi., 514.
(*f*) Huppart, *Zeit. f. Physiol. Chem.*, xviii., 137.
(*g*) Max Cremer, *Zeit. f. Biologie*, xxix., 484.
(*h*) E. Gibson, *Chem. Centralbl.*, 1893, ii., 530.
(*i*) Cross, Bevan, and Beadle, Chem. News, lxvii., 236.
(*j*) Brown and Morris, *Journ. Chem. Soc.*, liii., 604.
(*k*) Stone and Jones, *Agricultural Science*, vii., 6.
(*l*) Ebstein, *Archiv. f. Patholog. Anatomie*, cxxix., 451.
(*m*) E. Salkowski, *Centralbl. f. Med. Wissenschaft*, 1893, 193.
(*n*) Flint and Tollens, *Landw. Versuch-Stationen*, xlii., 381.
(*o*) W. H. Krug, *Journ. Anal. and Appl. Chem.*, vii. 68.
(*p*) E. Hotter, *Chem. Zeit.*, xvii., 43.

(*q*) B. B. Ross, *Journ. Anal. and Appl. Chem.*, vii., 83.
(*r*) E. Nihoul, *Chem. Zeit.*, xvii., 500.
(*s*) B. Guillaume-Gentil, *Schweiz. Wochenschrift f. Pharm.*, xxxi., 225.
(*t*) Arminius Bar, *Chem. Zeit.*, xvii., 499.
(*u*) Delton, *Bull. Assoc. Belge. Chim.*, vi., 154.
(*v*) H. Jacobi, *Annalen d. Chem.*, cclxxii., 170.
(*w*) Bechamp, *Bull. Soc. Chim. de Paris*, [3], ix., 401.
(*x*) B. Tollens, *Berichte der Chem. Gesell.*, xxvi., 1799.

OBITUARY.

PROFESSOR HERMANN LUDWIG FERDINAND VON HELMHOLTZ.

IT is perfectly needless to say how painfully the loss of this illustrious *savant* is felt, not alone in his own country, but throughout the civilised world. The deceased had completed his seventy-third year, having been born in 1821 at Potsdam, where his father was a teacher at the Gymnasium. His mother was an English woman, so that we may regard him as in part our kinsman. He studied medicine at Berlin, and after a short connection with one of the hospitals of that city he became an army-surgeon. Here already, amidst his official duties, he entered upon those physical researches which have made him so famous. In his twenty-seventh year he was promoted to the Chair of Anatomy at the Academy of Arts. The Chair of Physiology at the University of Königsberg shortly afterwards becoming vacant, he was elected to this office. In 1855 he was called to fill the Chair of Anatomy and Physiology at the University of Bonn. Three years subsequently he became Professor of Physiology at Heidelberg. The fact that his services were in such demand proves how rapidly and how widely his reputation had extended. In 1871 he succeeded to the Chair of Physics in the University of Berlin, a post which he held until the last few years.

Helmholtz was that very rare phenomenon, a master both in physics and in biology. Men who are dabblers in both these disciplines are unfortunately not rare, yet it is very unusual to find good work in both emanating from the same mind. The two sciences have, indeed, regions of contact which will prove fruitful. But in general we find that the observers and thinkers most attracted to the one are almost repelled from the other. It will be, perhaps, not forgotten that at the joint meeting of the British and the American Associations, held at Toronto, generalised photographs were taken, on the one hand, of the mathematicians and physicists, and, on the other, of the naturalists or biologists. A very striking difference between the two was recorded.

Perhaps Helmholtz was the most successful in the theory of light and colour. With Young he recognised, as the three primary colours, red, violet, and green. His discovery of the ophthalmoscope has proved of immense utility in the recognition and treatment of diseases of the eye, and has substituted accurate knowledge for loose conjecture. He was great also in the theory of sound. In 1875 there appeared his epoch-making work, "Sensations of Tone (*Ton empfindungen*) as a Physiological Basis for the Theory of Music."

In electricity, also, Helmholtz accomplished valuable work, though of less striking a character than what he has left us in optics and acoustics.

One of his earliest works was a treatise on the Conservation of Energy, which at once made him famous. In short, we can scarcely pronounce it an exaggeration when a contemporary remarks that he had done enough to make half-a-dozen celebrities.

NOTICES OF BOOKS.

The Scientific Foundations of Analytical Chemistry presented Elementarily. By W. OSTWALD. (Die wissenschaftlichen Grundlagen der analytischen Chemie, elementar dargestellt). Leipzig: W. Engelmann. 1894. Small 8vo., pp. 187.

THIS work takes up a position hitherto almost vacant, It does not put forward a series of procedures novel, or at least improved, but it enters upon questions which have been too much neglected. The author urges that the scientific elaboration of analytical chemistry is, even in the best text-books, confined to an exposition of the formulæ equations according to which the desired reactions should take place *in an ideal outside case.* "But that in fact there occur in general, instead of the intended complete reactions, incomplete changes, leading to states of chemical equilibrium, that there are no substances absolutely insoluble, and that there are no absolutely exact methods of separation and determination are circumstances which not merely too often escape the pupil, but which, I fear, are not so clearly present in the consciousness of the experienced analyst as it might be desired on behalf of a real decision on analytical methods and results."

In all these charges there is far too much truth. Yet if we compare, *e.g.*, the instructions for the determination of sulphuric acid in manuals of the present day with those recognised thirty or forty years ago, we shall see that many of the possible sources of inaccuracy are not merely recognised, but, where possible, guarded against.

Prof. Ostwald further complains that analytical chemistry still makes use of obsolete theoretical views, and does not hesitate to state the constituents of potassium sulphate as K_2O and SO_3.

The work is divided into two parts, Theory and Applications. In the former the author discusses the recognition of substances and the separation of substances by physical and chemical methods. Here we find the theory of solution and the account of the condition of dissolved bodies based upon the view of Arrhenius, that saline substances do not exist *as such* in aqueous solutions, but more or less completely split up into their constituents, the ions. The author then discusses chemical equilibria, the course of chemical procedures, and reactions with the liberation or the absorption of gases and the influence of the condition of ions. Lastly, we come to the quantitative determination of substances, or, as the author terms it, their *measurement.*

In the part treating of Applications Prof. Ostwald does not enter into details of treatment, but lays down general principles for the analysis of compounds belonging to the groups of the system of Mendeleeff, and to the non-metals. The remarks on the theory of indicators will be found very valuable.

To the more advanced student, and to the analytical practitioner, this book will prove most valuable. As the author says, in his Preface: "I have not made it my object to teach the beginner analytical chemistry as such." . . . "The book is to induce the reader to submit what he has learnt practically to a deeper consideration regarding its scientific foundation, so as to have it more freely and accurately at command." As an essentially novel feature, Prof, Ostwald considers the reference to the state of ions which may be assumed by the elements to be sought.

A New System of Chemical Notation and Nomenclature. Proposed by T. K. GAJJAR, B.Sc., M.A. Bombay: The Education Society's Steam Press. 1894.

MOST of our readers will no doubt have heard of the "Comic History of England" and the "Comic Latin Grammar"; but few, if any, have seen a "Comic

Chemistry." Chemistry is not a subject which readily lends itself to puns and jokes, though the late Mr. Brough made some very amusing sketches illustrating a well-known system of notation. The pamphlet now before us is, without any such intention on the part of its author, distinctly funny.

Mr. Gajjar's aim has been to provide an international notation (a kind of chemical Volapuk) which will be as readily understood by a European as by an Oriental; to this end he takes the classification of the elements, based on the Periodic Law of Newlands and Mendeleeff, and applies to them symbols in the Devanagari dialect, with their equivalents in English; the numerals are also designated by a system of vowel sounds. This is all very well, and works out in an entirely intelligible manner; but when we arrive at the final results (however dry and serious they may appear to an Indian student), our risible faculties overcome us and our smile broadens into a laugh. What professor of chemistry could possibly keep order in a class if—wishing to mention the elements, T, Si, Mo, Zn, Mg—he were to gravely (?) say to his students Sum, Dam, Rum, Jim, Jam? these being their names in the proposed nomenclature. Ingenious as the idea is, and however successful it may be in India, Mr. Gajjar's scheme is impossible for England.

Practical Work in General Physics, for Use in Schools and Colleges. By W. G. Woollcombe, M.A., B.Sc. Oxford: The Clarendon Press. 1894.

In the Introduction to this book the author emphasises the comparatively small value of mere book knowledge in any of the experimental sciences, and urges all students to make themselves thoroughly acquainted with the practical side of the subjects they are studying. The old maxim, that "an ounce of practice is worth a pound of theory," though not always applicable, is, we think, very near the truth. If a man learns to observe accurately, his work, with rough instruments, will be more trustworthy than that of a less experienced worker with more elaborate appliances. The better the instrument, the harder it is to do justice to it.

A list of some fifty experiments is given, with full directions as to carrying them out; they include simple ones, such as measurements of lengths, areas, and volumes, as well as those of a more advanced character. The possible and probable errors of observation are pointed out, as well as the best means of obviating them. The book is well written, and is not too technical.

Beginner's Guide to Photography: showing how to Buy a Camera, and how to Use it. Published by Perken, Son, and Rayment, London. Fifth Edition, Revised and Enlarged.

To those about to take up the pursuit of Photography some very good advice is given as to the choice of apparatus. Photographs (of a kind) can no doubt be taken with cheap and imperfect cameras, but to turn out results of any merit it is necessary to have appliances which are good and of a reasonable size, though not necessarily of great cost. One of the most important items is the lens; though good work can be done with a good lens and a poor camera, nothing satisfactory can be achieved with a bad lens, be the rest of the apparatus ever so good. The whole process and practice of photography is herein fully described, and every kind of apparatus is illustrated and priced; but owing to an unfortunate oversight, no doubt caused by the enlargement of this edition, all the references to the pages on which the illustrations are given have been wrongly numbered: this must be corrected in a subsequent edition. The table of "exposures," on page 119, is bound to be of great service to amateurs, and beginners might do worse than obtain a copy of the book.

Notes on Metallurgical Analysis. By Nathaniel W. Lord, E.M., Professor of Mining and Metallurgy at the Ohio State University. Columbus, Ohio. 1893.

These notes were written for the use of the students in the metallurgical laboratory of the Ohio State University, and give, in a condensed form, the methods selected to make up the course of study. No attempt is made to describe general reagents or apparatus, students taking up this course naturally being supposed to be familiar with such details.

The course deals principally with the production of the commoner metals, such as iron, copper, lead, zinc, &c., together with the materials used and the waste products formed in their manufacture.

The book is written in just the style most suitable to students; but we are sorry to note that its excellence is greatly marred by a very large number of Errata, most of which are of an important character, and further, even in the Errata themselves, there are no less than four references wrongly given.

CORRESPONDENCE.

THE ATOMIC WEIGHT OF CARBON.

To the Editor of the Chemical News.

Sir,—Mr. Matthewman has fallen into a not unnatural error, which I hasten to correct. My recent paper read to the Chemical Section of the British Association ended as follows:—

"Further particulars of the investigation, which has occupied nearly two years, are to be read in the *Philosophical Magazine* for the month of May last,* to which reference may be made."

I find no fault with Mr. Matthewman for not reading the May number of the *Phil. Mag.*, and I say, further, that if there had been an adequate discussion in the Chemical Section the essential facts would have come out. Unfortunately, however, the discussion was quite inadequate, and only a part of the facts came out.

When the *Phil. Mag.* paper is consulted it will be seen that, in addition to the half-carbon terms mentioned in the brief paper read to the Chemical Section, there are whole atom terms and that our investigation exhibits an ascending series of hydrocarbons wherein the increment is 7; that is to say, 6 parts of carbon and 1 part of hydrogen. Under these circumstances the legitimate conclusion is that the true carbon atom is 6.—I am, &c.,

J. Alfred Wanklyn.

THE INFLUENCE OF MOISTURE ON CHEMICAL COMBINATION.

To the Editor of the Chemical News.

Sir,—In the Chemical Section of the British Association meeting at Oxford, one of the most interesting events was the demonstration and discussion of the Influence of Moisture on Chemical Change. The paper, and experiments of Prof. J. T. Thomson, Mr. Brereton Baker, and Dr. Swan brought together a number of facts of an exceedingly suggestive nature, which showed that we are far from understanding the causes of some of the most familiar cases of chemical change. The discussion, however, did not do much to clear up the difficulties of the subject. It seems probable to the writer that moisture may play many parts, and influence different varieties of chemical change in different ways.

If we take the striking discovery of Mr. Baker, that

* "The Method of Fractional Distillation, Illustrated by the Investigation of Kerosene," by J. Alfred Wanklyn and W. J. Cooper.

ammonia gas and hydrogen chloride do not combine when mixed together in perfectly dry condition, it might be well to consider how far this behaviour is an example of the old adage, "Corpora non agunt nisi soluta,"—that is, whether the moisture does not act here chiefly as a solvent, breaking up the aggregation of molecules of ammonia gas and hydrogen chloride gas, and thus bringing about the combination with each other. This would be parallel to the action of water on a mixture of tartaric acid and carbonate of soda. We know that there is no reaction, however finely powdered and well mixed together these substances are, till water is added. It may be objected that water in its liquid state is here compared with a mere trace of the same element in the state of vapour. It would seem not unlikely, from the experiments of Dr. Bailey, that water vapour has the power of dissolving the chlorides of strontium and calcium, and carrying away with it portions of those salts when solutions of them are evaporated.

According to my theory, therefore, the mixture of dry ammonia gas and dry hydrogen chloride would consist of congeries of molecules of these respective compounds with little attraction for each other. The action of the trace of moisture would be to split up some of these congeries and bring certain single molecules sufficiently near each other for their mutual attraction to exert itself, and ammonium chloride would result. The molecular equilibrium of the mixture would then be disturbed, and the feeble attraction of the aggregation of molecules of ammonia and hydrogen chloride would then probably be sufficient to determine their combination, just as a gas, which at first offers considerable resistance to an electric discharge, will allow even a feeble one to pass through it when once its resistance has been overcome.—I am, &c.,

W. H. Pendlebury, M.A.

Dover College.

ELECTRO-SANITATION.

To the Editor of the Chemical News.

Sir,—Now electric currents are being recommended for the treatment of sewage and of other putrescible organic refuse it would be well if the authors of such schemes would inform the public more definitely of the composition and general properties of "electrozone." Will the refuse after treatment retain any manurial value, or will it be disposed of in pure waste?—I am, &c.,

J. W. S.

PHOTOGRAPHY OF THE BUNSEN FLAME REACTIONS IN THE ULTRA-VIOLET SPECTRUM.

To the Editor of the Chemical News.

Sir,—The apparatus described in the Chemical News, vol. lxx., p. 103, in connection with this subject can hardly be credited to Messrs. Eder and Valenta, as a full description and sketch by Mr. H. W. Wiley appeared in the *Journal of the American Chemical Society*, xv., p. 121, 1893, as a lamp for constant monochromatic light.—We are, &c.,

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Glasgow and West of Scotland Technical College.—Mr. H. G. Thorpe, B.A., Assoc. G. and W. of S. T. C., Senior Assistant of Prof. Sexton in the Metallurgical Department of the Technical College, has just been appointed Manager of the Extraction Works of the Kangarilla Mining Company. He is succeeded as assistant by Mr. John Buchanan, an old student of the College, and late of the Freiberg School of Mines.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académi des Sciences. Vol. cxix., No. 8, August 20, 1894.

Action of Halogenous Hydracids upon Formic Aldehyd in presence of Alcohols.—Louis Henry.—The author, referring to C. Favre's paper (*Comptes Rendus*, July 23, 1894, p. 284), on the "Condensation of Formic Aldehyd with the Alcohols of the Fatty Series in presence of Hydrochloric Acid," points out that he has been engaged with this subject for several years. The author's son, Paul Henry, mentions in 1891 the reaction discussed in C. Favre's paper. In the author's memoir (*Bull. de l'Acad. des Sciences de Belgique*, vii., p. 150) he has shown not merely the action of hydrochloric acid, but also that of hydrobromic and hydriodic acids.

Action of Camphoric Anhydride upon Benzene in presence of Aluminium Chloride.—E. Burcker and C. Stahl.—The authors have isolated the phenylcamphoric anhydride, $C_{16}H_{18}O_2$. They have also obtained a biphenylic compound, $C_{22}H_{24}O_2$. It is more soluble in benzene than phenylcamphoric acid, and separates from the solvent in the state of reddish yellow crystalline masses. The composition of these crystals is that above mentioned.

Extraction of Free Acid from Bees'-wax.—T. Marie.—The cerotic acid of Brodie has been shown by Schalfesew to be a mixture. Crude cerotic acid, though described as cerotic acid, contains from 30 to 40 per cent of analogous acids. The residues obtained in the purification of cerotic acid yield melissic acid identical with that which Story-Maskelyne and Pieverling obtained from carnauba wax.

Chemical Constitution of the Atmosphere.—Dr. T. L. Phipson.—The author adds an appendix to his memoir on the "Origin of Atmospheric Oxygen (*Comptes Rendus*, August 7, 1893). He holds that the primitive atmosphere consisted of nitrogen, carbon dioxide, and watery vapour. In this mixture certain plants (*Convolvulus arvensis*) are capable of vegetating perfectly and gradually liberate oxygen by decomposing the carbon dioxide.

No. 9, August 27, 1894.

This issue contains no chemical matter.

Journal fur Praktische Chemie.
New Series, Vol. l., Nos. 13 and 14, 1894.

Condensation of Aldehyds and Cyanides.—C. Beckert.—Already inserted.

Communications from the Laboratory of the University of Freiburg.—A continuation of a paper by Ad. Claus and Alf. Ammelburg, on meta-ana-dibromquinoline.

Regularities of Boiling- and Melting-Points.—G. Cohn.—A collection of twenty-seven tables, incapable of abridgment. The ketones whose alkyls have an even carbon number melt, on the average, 7·9° lower than the acids belonging to them; but the ketones whose alkyls have an uneven carbon number, of about double the value (14·6°) lower than such acids. By means of these constants we can calculate the melting-points of analogous unknown ketones.

Researches from the Chemical Laboratory of Prof. Alex. Saytzeff, of Kasan.—This comprises papers by J. Lebedeff, on the transformation of elaidic acid into iso-oleic and oleic acids; by M. Saytzeff, on the conversion of brassidic acid into iso-erucic and erucic acids; by M. Joukowsky, on the oxidation of brassidic

acid with potassium permanganate in an alkaline solution; by S. Talanzeff, on the history of behenic acid; by M. C. and Alex. Saytzeff, on the action of sodium bisulphite and sulphurous acid upon oleic and erucic acids; and by Alex. Saytzeff, on the constitution of oleic and erucic acids and their isomers.

The Benzene Nucleus.—W. Vaubel.—A critique of Bruhl's work on the relations of the bonds in benzene, and on A. von Baeyer's recent communication on the optical activity of limonene. The paper requires the accompanying diagrams.

On the Determination of Vapour-Densities, and on a Method of Exhaustion without an Air-Pump or a Water-Sprengel.—C. Schall.—This paper requires the two accompanying figures.

On Ortho-oxy-diphenylamine.—Dr. A. Deninger.—To obtain this compound, not yet described, the author heats 50 grms. aniline and 59 grms. pyrocatechin, with 25 grms. calcium chloride and a little carbonic acid, to 180° for twenty-four hours, in an autoclave.

On Synthetic Experiments by means of Sodium and Nitriles.—R. Walther.—On the action of 2 mols. sodium upon 3 mols. nitrile, dissolved in ether or benzene, there are formed dinitriles, and at the same time sodium cyanide and a hydrocarbon. The author extends this reaction by using, in place of the third mol. of nitrile, a substance which may be expected to react in the direction desired.

On Potassium Chlorochromate.—G. Herfeldt.—The author has attempted to obtain chlorochromic anhydride, but without success.

Constitution of the Aniline Compound of Glucose.—S. Marchlewski.—The author is attempting to obtain apposition products of glucosides with hydrocyanic acid.

MISCELLANEOUS.

Schools of Chemistry, &c.—The following additional information arrived too late for insertion in the STUDENT'S NUMBER:—

CITY OF LONDON COLLEGE, White Street, Moorfields, E.C.—The Forty-Seventh Session will commence Oct. 1st. Lectures and Laboratory Instruction in Chemistry and Experimental Physics by Mr. Isaac Sydney Scarf, F.I.C., F.C.S., assisted by Mr. J. Davis, Int. B.Sc. Lond., and Mr. H. V. Buttfield, F.C.S.

An Epidemic among Trout. — R. Emmerich and E. Weibel describe, in the *Archiv Hygiene*, an epidemic produced by a micro-organism probably identical with Zimmermann's *Bacillus devorans*. — *Chemiker Zeitung Repertorium*.

Bacteriological Examination of Potable Water.—International Congress for Applied Chemistry, held at Brussels and Antwerp: in Section C the reporter, Dr. E. Malvoz, discussed the relation between the presence of microbia and pollution by nitrites and ammonia. He has observed that though the absence of nitrites and ammonia is no proof of the bacteriological purity of water, yet inversely nitrites and ammonia are almost invariably present only in waters containing many bacteria of various kinds. Concerning the presence of *Bacterium coli* in water, the author had observed that this micro-organism is present in water only when pollution by the soil or the air is probable. The presence of *Bacterium coli* allows us to infer a contact—direct or indirect—of the water and human excreta. The author rejects the determination of the sum total of microbia present, as it throws no light on the properties of the water, and may give scope to misinterpretations. It was concluded that the hygienic value of a water, as regards its total number of micro-organisms, depends on local conditions, such as the source of the water, the method of its conveyance to the place of consumption, the character of the soil, &c. —*Chemiker Zeitung*.

The Chemical Laboratory of Wiesbaden.—In the Summer Term, 1894, there were sixty-six students on the books. Of these, forty-one were from Germany, seven from England, three from the United States of America, two from Switzerland, two from Holland, two from Belgium, two from Russia, and two from Norway; also one from each of the following countries — Austro-Hungary, Denmark, Sweden, Italy, and Australia. Besides the Director, Geh. Hofrath Prof. Dr. R. Fresenius, there are engaged, as teachers in the establishment, Prof. Dr. H. Fresenius, Prof. Dr. E. Borgmann, Dr. W. Fresenius, Dr. E. Hintz, Dr. med. G. Frank, Dr. Lenz, and architect T. Brahm. The assistants in the instruction laboratory were three in number, in the private laboratory twenty, and in the Versuchsstation two. The next Winter Term begins the 15th of October. During the last term, besides the scientific researches, a great number of analyses were undertaken in the different departments of the Laboratory and the Versuchsstation, on behalf of manufacture, trade, mining, agriculture, and hygiene.

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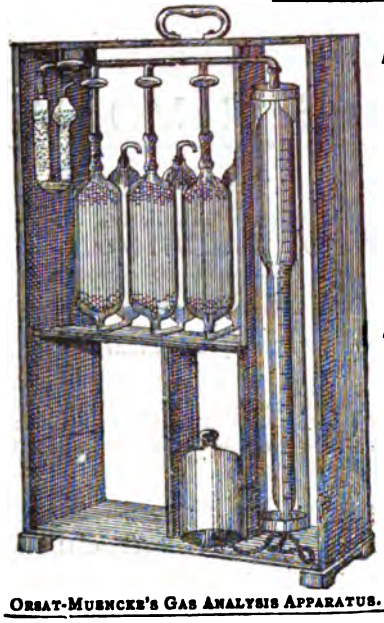

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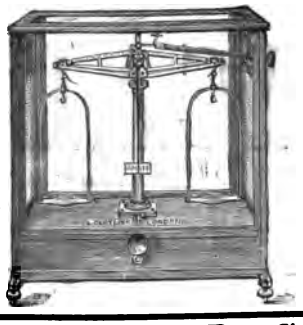

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THE CHEMICAL NEWS.

Vol. LXX., No. 1818.

NOTES ON WATER ANALYSIS.

By C. A. SEYLER, B.Sc.

(Continued from p. 141).

III. *Dissolved Oxygen.*

For technical purposes a method of estimating free oxygen must fulfil the following conditions:—It must be simple, speedy, and accurate, and must not require large quantities of water. This practically limits us to volumetric methods. A further condition is that the water must not be subjected to a diminished oxygen pressure, *i.e.*, must not be carried out in an atmosphere of inert gas, otherwise there might be, according to the experiments of Roscoe and Lunt, a rapid loss by diffusion.

Two methods at least fulfil these requirements, those of Thresh (*Journ. Chem. Soc.*, March, 1890) and Ludwig Winkler (*Ber.*, 1888, s. 2843). I can confirm the accuracy of both these methods, which give identical results.

For purposes of checking the accuracy, water saturated by agitating with air at a given temperature is best, bearing in mind the fact that water can easily remain supersaturated with a rising temperature. It is also important to note that numerous experimenters of repute, Roscoe and Lunt, Dittmar, Pettersen, and Winkler, have found Bunsen's numbers for the solubility of oxygen too low, even to the extent of 10 per cent. Roscoe and Lunt (*Journ. Chem. Soc.*, 1889, vol. i., p. 552) give complete tables agreeing well with other determinations.

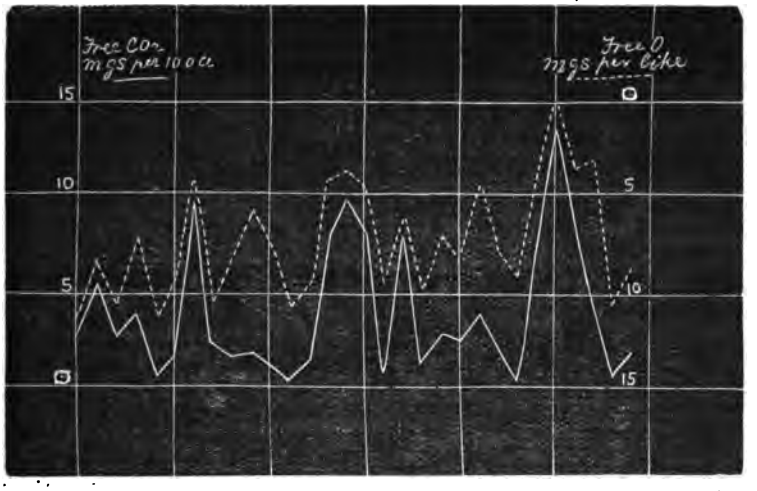
Of the two methods, Winkler's is much the simpler, requiring no apparatus and chemicals but what are found in every laboratory. In this method manganous hydrate serves as the oxygen-carrier, and enables it to liberate its equivalent of iodine, which is then titrated. The solutions required are as follows:—

(1) 40 grms. $MnCl_2.4Aq$ (free from iron) dissolved in water and made up to 100 c.c.

(2) 32 grms. sodic hydrate (free from nitrite) and 10 grms. KI made up to 100 c.c. with water.

A narrow-mouthed well-stoppered vessel, holding a known volume of water, is required. The cylinders used by Thresh and holding 252 c.c. are convenient. The vessel is filled by a syphon, and 1 c.c. of each of the above solutions introduced by a pipette with long stem, so as to flow to the bottom, displacing 2 c.c. of the water from the top. The stopper is then inserted so as to be quite free from air bubbles, and the contents mixed by shaking. The precipitated manganese hydrate becomes brown if free oxygen is present, and soon sinks to the bottom. 5 c.c. of strong HCl are then introduced by a pipette reaching just above the layer of precipitate, the clear alkaline solution only being displaced from the top, the stopper again inserted, and the vessel shaken. When the precipitate is entirely or nearly dissolved the yellow solution is run into a flask and titrated with thiosulphate in the usual manner. If 250 c.c. of water be used Thresh's thiosulphate equivalent to 0·25 m.grm. of oxygen is convenient, each c.c. then representing 1 m.grm. per litre. This contains 7·75 grms. of sodic thiosulphate per litre. The great inconvenience is that it rapidly loses strength. I find that the suggestion of Harcourt and Esson to add a little caustic soda to the solution is wonderfully efficacious, 4 c.c. of N caustic soda added before making up to a litre renders the thiosulphate perfectly stable for months, if not kept exposed to the light. It then needs only occasional standardising by means of a standard solution of bichromate.

If nitrites are present they may interfere with the titration, acting as oxygen-carriers, and causing a continuous liberation of iodine. This may be obviated by titrating in a current of coal-gas, exactly as in Thresh's method, but if the amount of nitrite is not large, and the first disappearance of the blue tint be taken, the titration in coal-gas will not differ appreciably. If much nitrite is present it must be estimated and corrected for, but this is a very rare case. It has been objected that iodometric methods are inapplicable to waters containing much organic matter, as this may absorb iodine. I do not find this objection well grounded. In the extreme case of sewage effluent, no iodine was absorbed in one case, and in another, where some SH_2 was present, the absorption only corresponded to 0·7 c.c. per litre, and could easily be estimated and a correction applied.



Pure Surface-waters.—As proved by the experiments of Gill (*Journ. Anal. Appl. Chem.*, vi., No. 11) and myself (Chem. News, lxvii., p. 87) water can readily be supersaturated to a very large extent. This applies even to surface-waters as shown by the following example—the water of a reservoir 22 feet deep:—

Temperature of water, 14·75° C.; of air, 14·5°. Dissolved oxygen, 8·01 c.c. per litre; saturated at 8·5° C. (Roscoe and Lunt), 6·5° below the temperature of the water. As a check, air was now blown through the same water at 15·5° C., and the oxygen found was 6 98 c.c. per litre, saturated at 15° according to Roscoe and Lunt.

Nevertheless, the amount of dissolved oxygen in surface-waters follows the average temperature of the air. This is proved by graphically plotting the average monthly temperature, and the average temperature of saturation of surface-waters during that month. The curves follow each other pretty closely, rising steadily from a minimum about January to a maximum about August, and decreasing suddenly in September or October. From results obtained in 1893, I find that the average temperature at which the surface-waters would be saturated was above that of the average atmospheric temperatnre, except from about July to October, when the waters were generally saturated at a lower temperature.

Underground waters, as a general rule, are characterised by low dissolved oxygen, the amount bearing no obvious relation to the temperature of the season. In a previous note attention was drawn to the fact that the amount of free oxygen is related to the amount of *free* carbonic acid. This is shown by the accompanying diagram, representing thirty waters taken at random. The broken line represents oxygen deficit. The best definition of oxygen deficit is the deficiency from saturation at the temperature indicated by the amount of nitrogen, but in the absence of this I have taken, for purposes of illustration, the deficit from the maximum solubility, *i.e.*, at 0° C., taking this in round numbers as 15 m.grms. per litre. The general correspondence of oxygen deficit with free CO_2 is apparent, but is not absolute. What interpretation is to be put upon it is a matter for further experiment. The oxygen deficit and free CO_2 increase with the depth in the same well (see B. Fischer, *Zeit. Hyg.*, xiii.; R. Lepsius, *Ber.*, 1885, s. 2487). In deep wells only traces of oxygen are found. Probably the chief cause of the correspondence is diffusion at the surface exposed to the ground air, and this makes it interesting to compare the rate of gain of oxygen and loss of CO_2.

In a water shown by the presence of free CO_2 and little organic matter to be a ground-water, a small amount of dissolved oxygen will be a good rather than a bad sign, as indicating that the water has come from a depth.

ON THE ASSUMPTION OF A SPECIAL "NASCENT STATE."

By LAUNCELOT ANDREWS, Ph.D.

The assumption frequently appears in chemical literature that elements at the moment of being set free from their compounds exhibit properties which the same elements do not ordinarily possess. This alleged specific condition is designated as the "nascent state," or *status nascendi*. The hypothesis of such a condition dates back to the time when the dualistic theory held sway, and, so far as I am aware, has not been subjected to criticism in the light of modern views.

It is my purpose in the present paper to consider the following pertinent questions concerning this hypothesis:—

1. Is it necessary to our understanding of any known facts?
2. Does it offer a simpler explanation of any facts than can be given without its aid?
3. Is it inconsistent with known facts?
4. Can it be consistently applied to any class of phenomena without the aid of additional auxiliary assumptions?

One of the classes of chemical reactions which is most often explained by the assumption of a nascent state, is that in which reduction is effected by metallic zinc in acid solutions or by sodium amalgam in aqueous, neutral, alkaline, or acid solution, or by other oxidisable metals. Here the metal is said to act upon the water or the acid setting free hydrogen, which in turn, by virtue of the peculiar properties it is supposed to possess in the nascent state, effects the reduction.

Thus the reducing of ferric chloride to ferrous chloride by zinc in acid solutions would be represented by the following two equations:—

$$Zn+2HCl=ZnCl_2+H_2 \quad [1$$

$$2H+2FeCl_3=2FeCl_2+2HCl \quad [2$$

The reduction of a copper sulphate solution would be represented thus:—

$$H_2SO_4+Cu=CuSO_4+2H \quad [3$$

$$2H+CuSO_4=Cu+H_2SO_4 \quad [4$$

And in the same way the reduction of metallic Cu at the negative electrode during the electrolysis of a $CuSO_4$ solution would be represented as *secondary* and due to the nascent hydrogen appearing there. In the familar process of preparing sulphurous anhydride by the action of copper on concentrated hot sulphuric acid, we find it assumed that hydrogen is first produced as in Equation 3, and then in *statu nascendi* immediately reacts on the sulphuric acid.

$$Cu+H_2SO_4=CuSO_4+H_2 \quad [5$$

$$2H+H_2SO_4=2H_2O+SO_2 \quad [6$$

forming water and sulphurous anhydride.

Many other cases might be cited of simple reactions in which it is considered necessary by some authors to employ the nascent hypothesis, but I shall, for the present, confine myself to these, and in the light of the facts seek an answer to our four crucial questions. If we dispense with the hypothesis, we must assume in each case a direct action of the metal on the salt; thus zinc and ferric chloride would give zinc chloride and ferrous chloride.

$$Zn+2FeCl_3=ZnCl_2+2FeCl_2 \quad [7$$

Zinc and copper sulphate would simply present a case of direct interchange of metals.

$$Zn+CuSO_4=ZnSO_4+Cu \quad [8$$

The reduction of copper by electrolysis would be primary, not secondary.

To negative pole. To positive pole.

$$Cu \leftarrow CuSO_4 \rightarrow SO_3+O \quad [9$$

This view in the latter case will not be seriously questioned by any student of the recent work of Arrhenius and Ostwald and their followers.

Lastly, we can simply represent the reduction of hot concentrated sulphuric acid as consisting in the first stage in an oxidation of the copper at the expense of the acid.

$$Cu+H_2SO_4=CuO+\overbrace{H_2SO_3}^{H_2OSO_2} \quad [10$$

The sulphurous acid becoming dehydrated, of course, at the high temperature of the reaction; and the copper oxide being soon converted into copper sulphate.

In the cases named it is clear that the nascent state hypothesis is not necessary and does not lead to a simpler explanation of the facts than can be had without it. Is it inconsistent with any of the facts? Considering first the reduction of sulphuric acid by copper, the following phenomena may be observed:—When metallic copper, carefully cleaned, is heated gradually with concentrated sulphuric acid until sulphurous anhydride begins to be evolved, the surface of the copper becomes coated with a black crust. If the metal is now removed from the acid, then washed and placed in hydrochloric acid, the coating dissolves, forming a solution of copper chloride. In fact, this crust consists of copper oxide. Its formation is not explained by the hypothesis in question (Eqs. 5—6), but is a direct confirmation of Eq. 10. If the acid is reduced by hydrogen, some of the hydrogen might be expected to escape unoxidised. In order to test this point, pure sulphuric acid was heated with copper which was obtained by electrolysis from a re-crystallised specimen of copper

sulphate and subsequently ignited in an atmosphere of carbon monoxide. The gases evolved were collected over mercury, and about 50 c.c. were treated with caustic potash. All was absorbed except a small bubble, which consisted essentially of oxygen. No hydrogen could be detected.

In order to demonstrate, however, that none had been formed, it was necessary to show that if formed it would not be wholly oxidised by the hot acid. To get direct evidence upon this point, a quantity of nearly pure zinc was heated with the same acid that had served for the copper experiment, and in the same way. Fifty c.c. of the evolved gas was only partly absorbed by potash, a residue of about 3 c.c. being left. This residue consisted essentially of hydrogen.

The chain of evidence now appeared complete, for unless there were two kinds of nascent hydrogen it would be all oxidised in both cases *if in either*, the conditions being the same, and the fact that none was found in the copper experiment must be taken for valid proof that none was formed.

In reality the correct view would appear to be that at the temperature of the reaction the acid is for the greater part dissociated into H_2O and SO_3, the copper being oxidised by the latter only. The zinc acts upon the SO_3, forming SO_2, and also upon the undissociated part of the acid, setting free hydrogen, which escapes.

Further light may be thrown upon this matter by a consideration of the reduction of the sulphuric acid by carbon. This reaction takes place at about the same temperature as that with copper, in accordance with the equation—

$$C+2H_2SO_4=2H_2O+CO_2+2SO_2 \qquad [11$$

Here there can be no question of nascent hydrogen unless by assuming the existence of a sulphate of carbon, thus—

$$C+2H_2SO_4=C(SO_4)_2+4H \qquad [12$$

which is wholly unwarranted, and there is no ground for supposing the mechanism of the action of carbon on sulphuric acid to be entirely different from that of copper on the same compound.

A favourite field in which nascent hydrogen often disports itself lies in the extremely complex reactions between nitric acid on the one hand and various metals on the other. Here the nitric acid may be reduced to ammonia, hydroxylamine, free nitrogen, nitrous acid, any of the oxides of nitrogen, and possibly still other products. Often many of them are simultaneously formed. Of these, ammonia, and "laughing gas," and N_2 are never formed by the action of mercury, Bi, Cu, and Ag (*Ber.*, 92, 616, 898 f.). Iron, on the other hand, may reduce the whole of the nitric acid to ammonia. Montemartini, who has made a special study of this group of reactions (*loc. cit.*), and others have shown that the various metals reduce nitric acid in various ways, giving reaction products in different proportions and of different kinds. The bearing of this upon the subject of the present paper is evident. If, for example, iron, zinc, and copper all reduce nitric acid indirectly through the primary formation of nascent hydrogen, we would expect the ultimate products to be the same in kind and in relative amount, the absolute amount depending simply upon the quantity of hydrogen formed. Since this is not so, the conclusion is inevitable that the nascent hydrogen is not the reducing agent, but the action of each metal is immediate and specific, removing oxygen from the acid, and forming unstable intermediate products which elude direct observation, but which, by their reactions, give rise to the products characteristic of each case.

I have endeavoured in this discussion to select the fairest instances of the application of the nascent condition hypothesis, and find myself forced to the conclusion that it is the survival of an obsolete doctrine; that it explains nothing which cannot be as well or better explained without it; that it cannot be reconciled in certain cases with known facts; and that, therefore, we are not at present justified in the assumption that elements at the moment of formation or liberation from their compounds possess properties in any way different from those they commonly exhibit.—*Proc. Iowa Academy of Sciences*, Part 4.

ON THE COMPOSITION OF THE FEN SOILS OF SOUTH LINCOLNSHIRE.

By R. H. WILSON.

As the systematic investigation of soils of various parts of the country can hardly be over-estimated, it is a pleasure for me to give the composition of a number of soils from the Fens which I have recently determined. The soils were collected from the farm of Mr. T. Hardy, near Crowland, by the Lawes and Gilbert method. Each sample was taken to the depth of from 6 to 10 inches, being about the average depth cultivated. The samples for each analysis were prepared by the most careful methods, being thoroughly mixed, and finally made to pass through a sieve of 30 meshes to the linear inch. The following results were obtained from these soils, which were collected from six different fields of arable land:—

	No. I.	No. II.	No. III.
Moisture	19·61	12·70	7·27
*Organic matter and combined water	35·20	27·90	12·51
Ferric oxide	3·45	5·76	4·13
Alumina	4·18	4·77	7·32
Lime	1·20	1·00	0·87
Magnesia	0·30	0·50	0·13
Potash (K_2O)	0·08	0·07	0·08
Phosphoric acid (P_2O_5)	0·77	1·02	1·24
Sulphuric acid (SO_3)	0·45	0·52	0·16
Carbonic acid (CO_2)	1·05	0·47	0·89
Chlorine	0·03	0·03	0·01
Silica and insol. matter	33·68	45·26	65·48
	100·00	100·00	100·00
* Containing nitrogen	0·45	0·39	0·19

	No. IV.	No. V.	No. VI.
Moisture	17·73	8·55	13·60
*Organic matter and combined water	23·40	12·93	7·60
Ferric oxide	4·89	1·05	3·84
Alumina	4·89	5·98	2·01
Lime	1·24	1·09	2·00
Magnesia	0·21	0·39	0·40
Potash (K_2O)	0·11	0·08	0·09
Phosphoric acid (P_2O_5)	1·20	0·68	1·23
Sulphuric acid (SO_3)	0·15	0·15	0·20
Carbonic acid (CO_2)	0·72	0·72	2·91
Chlorine	0·03	0·01	0·02
Silica and insol. matter	45·43	68·37	66·10
	100·00	100·00	100·00
* Containing nitrogen	0·58	0·27	0·20

The specific gravities of these soils were ascertained to be the following:—

No. I.	1·62
No. II.	1·78
No. III.	2·21
No. IV.	1·82
No. V.	1·83
No. VI.	2·12

It is well known that the value of chemical analysis in deciding agricultural questions in connection with soils

(such as claying, subsoiling, liming, &c.), is often very great, and in many cases at once determines whether a proposed scheme for improvement is calculated to succeed or not. Besides, the infertility of a soil is often explained by a chemical analysis. The soil may be deficient in some substance indispensable to the growth of the crops, or it may contain something injurious to them; in either case an analysis is generally able to enlighten us, and to point out the means for remedying the evil.

The results of the analyses of the soils detailed in this paper show that they are of good quality, although in each case the potash is rather low—the average being 0·085 per cent—whereas in a first-class soil potash varies from 0·6 to about 1 per cent. Soils Nos. I., II., and IV. are rich in nitrogen; and all the samples are rich in phosphoric acid, the percentages varying from 0·68 to 1·24 per cent.

THE ACTION OF LIGHT UPON DYED COLOURS.*

During the past year the work of this Committee has been continued, and a large number of wool and silk patterns, dyed with various natural and artificial *orange* and *yellow* colouring matters, have been examined with respect to their power of resisting the fading action of light.

The general method of preparing the dyed patterns, and the manner of exposing them under glass, with free access of air and moisture, were the same as already adopted.

The patterns were exposed at Adel, near Leeds, in the grounds of James A. Hirst, Esq., to whom the best thanks of the Committee are again due for his kind permission to do so.

Each dyed pattern was divided into six pieces, one of which was protected from the action of light, while the others were exposed for different periods of time. These "periods of exposure" were made equivalent to those adopted last year, by exposing, along with the patterns, special series of "standards," dyed with the same colouring matters as were then selected for this purpose. The standards were allowed to fade to the same extent as those which marked off the "fading period" of last year, before being renewed or removing a set of dyed patterns from the action of light. The patterns exposed during the past year are therefore comparable, in respect of the amount of fading which they have experienced, with the red dyes already reported upon.

The patterns were all put out for exposure on June 8, 1893, certain sets being subsequently removed on the following dates:—July 1, July 31, August 26, 1893; February 19, June 12, 1894. Of the five "periods of exposure" thus marked off, periods 1, 2, and 3 were equivalent to each other in fading power, whereas periods 4 and 5 were each equivalent to *four* of the first period in this respect; hence five patterns of each colour have been submitted respectively to an amount of fading equal to 1, 2, 3, 7, and 11 times that of the first "fading period" selected—viz., June 8 to July 1, 1893.

The dyed and faded patterns have again been entered in pattern-card books in such a manner that they can be readily compared with each other.

The following tables give the general result of the exposure experiments made during the year 1893—94, the colours being divided, according to their behaviour towards light, into the following five classes: Very fugitive, fugitive, moderately fast, fast, very fast.

The initial numbers refer to the order of the patterns in the pattern-books. The S. and J. numbers refer to Schultz and Julius's "Tabellarische Uebersicht der künstlichen organischen Farbstoffen."

The colours marked thus (*) appear to be somewhat faster than the rest of the class in which they are placed.

In the case of colouring matters requiring mordants, the particular mordant employed is indicated in brackets after the name of the dye-stuff.

Class I.—Very Fugitive Colours. (Wool).

The colours of this class have faded so rapidly that at the end of the first "fading period" (June 8 to July 1, 1893) only a very faint colour remains, or it has become very materially altered in hue. At the end of the fifth period (one year) all traces of the original colour have disappeared, the woollen cloth being either quite white or merely of a yellowish or brownish tint.

Nitro Colours.

Wool Book III.

Acid Yellows.—

9. Aurantia. Ammonium salt of hexa-nitro-diphenylamine. S. and J. 14.
32. *Brilliant yellow. Sodium salt of dinitro-α-naphthol-α-sulphonic acid. S. and J. 12.
37. *Naphthol yellow. Sodium salt of dinitro-α-naphthol. S. and J. 9.
38. *Naphthol yellow S. Sodium salt of dinitro-α-naphthol-β-sulphonic acid. S. and J. 11.
43. Picric acid. Tri-nitro-phenol. S. and J. 1.

Azo Colours.

Wool Book IV.

Mordant Colours.—

14. *Wool Yellow (Cr.). From azo derivative of aniline and maclurin. S. and J. 32.

Wool Book III.

Basic Yellows.—

4. Chrysoïdine. From aniline and *m*-phenylene-diamine. S. and J. 31.

Direct Cotton Colours.—

1. Terra Cotta F. From primulin and *m*-phenylene-diamine-azo-naphthionic acid.
9. Direct Orange RR. Constitution not published.
26. Thiazol Yellow. From azo derivative of dehydro-thio-toluidine-sulphonic acid, and dehydro-thio-toluidine-sulphonic acid. S. and J. 98
28. Mimosa Yellow. From azo derivative of primulin, and ammonia.
30. Direct Yellow TS. Constitution not published.
36. Direct Orange R. Constitution not published.
39. Direct Yellow ASC. Constitution not published.

Diphenylmethan Colours.

Basic Colours.—

7. Auramine. Imido-tetra-methyl-diamido-diphenyl-methan-hydro-chloride. S. and J. 260.

Triphenylmethan Colours.

Acid Colours.—

48. Uranin A. Sodium salt of fluorescein. S. and J. 315.

Quinoline Colours.

Basic Colours.—

42. Quinoline Yellow (sol. in spirit). Quino-phthalone. S. and J. 378.

Acridine Colours.

Basic Colours.—

1. Acridine Orange R. extra. Zinc salt of tetra-methyl-diamido-phenyl-acridine.
2. Acridine Orange NO. Zinc salt of tetra-methyl-diamido-acridine. S. and J. 381.
3. Phosphine. Diamido-phenyl-acridine-nitrate. S. and J. 382.

* Report of Committee, consisting of Professor T. E. Thorpe (Chairman), Professor J. J. Hummel (Secretary), Dr. W. H. Perkin, Professor W. J. Russell, Captain W. de W. Abney, Professor W. Stroud, and Professor R. Meldola. (Drawn up by the Secretary). Read before the British Association (Section B), Oxford Meeting, 1894.

6. Benzoflavine. Diamido-phenyl-di-methyl-acridine hydrochloride. S. and J. 383.

Thiobenzenyl Colours.

Wool Book III.

Basic Colours.—

9. Thioflavin T. Dimethyl-dehydro-thio-toluidine-methyl chloride. S. and J. 384.

Acid Colour.—

29. Thioflavin S. Sodium salt of dimethyl-dehydro-thio-toluidine-sulphonic acid. S. and J. 385.

Direct Cotton Colour.—

31. Primulin. Sulphonated product of the interaction of sulphur and *p*-toluidine. S. and J. 386.

Natural Colouring Matters.

Non-mordant Colours.—

1. Annatto. Pulp from fruit of Bixa orellana.
2. Saffron. Stigmata of the flower of Crocus sativus.
3. Turmeric. Rhizome of Curcuma tinctoria.

Mordant Colours.—

1. Young Fustic (Al.). Wood of Rhus cotinus.
8. Tesu (Al.). Flowers of Butea frondosa.

Notes.—Certain of the nitro colours show extreme sensitiveness to light by rapidly altering in hue. During the first "period of exposure," the rich red-orange colour of Aurantia, for example, soon changes to brown, and the pure lemon-yellow of picric acid changes to orange-yellow; in both cases these altered colours fade slowly without any further change in hue, and might almost be placed among the "moderately fast colours." Brilliant Yellow, Martius Yellow, and Naphthol Yellow S behave somewhat like Picric Acid, but the alteration in hue is much less pronounced. Thiazol Yellow, Mimosa Yellow, Thioflavin T and S, and Primulin all fade rapidly during the first "period of exposure" to a yellow-buff, which then appears to be "moderately fast."

CLASS II.—FUGITIVE COLOURS. (WOOL).

The colours of this class show very marked fading at the end of the second "fading period" (July 1 to July 31, 1893), and after a year's exposure they have entirely faded, or only a tint remains.

Azo Colours.

Wool Book III.

Acid Colours.—

1. Orange R. From xylidine-sulphonic acid and β-naphthol. S. and J, 81.
6. Orange I. From *p*-sulphanilic acid and α-naphthol. S. and J. 72.
14. Narceïn. Sodium bisulphite compound of Orange II. S. and J. 103.
35. Phenoflavin. From *m*-sulphanilic acid and diamido-phenol-sulphonic acid.

Direct Cotton Colours.—

4. Benzo Orange R. From benzidine, salicylic and naphthionic acids. S. and J. 173.
5. Salmon Red. Sodium salt of diamido-diphenyl-urea-disazo-naphthionic acid. S. and J. 143.
6. Toluylene Orange R. From *o*-tolidine and *m*-toluylene-diamine-sulphonic acid. S. and J. 197.
8. Cloth Orange. From benzidine, salicylic acid, and resorcinol. S. and J. 170.

Quinoline Colours.

Acid Colours.—

41. Quinoline Yellow S. Sodium salt of quino-thalone-disulphonic acid. S. and J. 379.

Natural Colouring Matters.

Wool Book IV.

Mordant Colours.—

1. Tesu (Cr.).
3. Young Fustic (Cr.).
15. Anthracine (Cr.). Composition not published.
2. Quercitron Bark (Al.). Bark of Quercus niger.
3. Old Fustic (Al.). Wood of Morus tinctoria.
6. Flavin (Al.). Quercetin prepared from quercitron bark.
7. Persian Berries (Al.). Fruit of Rhamnus saxatilis.
2. Persian Berries (Sn.).
3. Young Fustic (Sn.).
4. Flavin (Sn.).
5. Quercitron Bark (Sn.).
6. Old Fustic (Sn.).
7. Tesu (Sn.).

Notes.—The fugitive character of Narceïn as compared with Orange II., of which it is merely the sodium bisulphite compound, is very pronounced. The bright orange of Flavin with tin mordant changes rapidly during the first exposing period to an olive-yellow, which may be regarded as "moderately fast." A similar change is noticed in the case of Quercitron Bark and Old Fustic with the same mordant, the faded colour of the latter being, however, very dull.

With aluminium and tin mordants Anthracine gives bright but very fugitive colours.

(To be continued).

THE GENERATION OF CHLORINE FOR LABORATORY PURPOSES.*

By F. A. GOOCH and D. ALBERT KREIDER.

THAT chlorine may be generated in a state of greater or less purity, variable with the conditions of evolution, by the action of hydrochloric acid upon potassium chlorate, has been shown by Pebal (*Ann. der Chem.*, clxxvii., 1) and Schacherl (*Ibid.*, clxxxii., 197), but the application of this fact to the practical generation of chlorine for the purposes of the laboratory has not to our knowledge been proposed. The desirability of an automatic generator from which an abundant flow of chlorine gas may be drawn at will or shut off without danger or inconvenience has led us to a study of the conditions most favourable to the safe evolution of chlorine by the action of the chlorate.

Pebal (*loc. cit.*) showed that the gas evolved at ordinary temperatures from a mixture of potassium chlorate and sodium chloride acted upon by sulphuric acid diluted with twice its volume of water consists of chlorine and chlorine dioxide in nearly equal proportions. Schacherl (*loc. cit.*) found that when potassium chlorate was acted upon by hydrochloric acid diluted with twice its own volume of water the yield of chlorine was about 46 per cent or 57 per cent of the mixed gases, according as the chlorate was granular or in fine powder; that hydrochloric acid of half strength yielded a gas containing nearly 60 per cent of chlorine, and that the proportion of chlorine rose nearly to 68 per cent when the gas was passed through concentrated hydrochloric acid and then washed with water; that the chlorate when acted upon by the strongest hydrochloric acid cooled to 0° C. and then warmed only enough to start the action, yielded a gas carrying 87 per cent of chlorine; and that when a solution of potassium chlorate was permitted to flow into hot strong hydrochloric acid the free chlorine constituted nearly 75 per cent of the mixture. So it appears that the highest yield of chlorine resulted when the solution of the chlorate entered gradually the hot strong acid—a condition not easily attained in an automatic generator.

The fact that chlorine dioxide is so easily decomposed by heat into chlorine and oxygen naturally suggests the possibility of increasing the proportion of chlorine evolved in the first instance by working at the highest temperatures practically attainable under the conditions. In order, however, to secure a temperature approaching the boiling-point of water it is necessary to reduce somewhat

* Contributions from the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, xlviii., August, 1894.

the strength of the hydrochloric acid acting (in order to avoid the evolution of hydrochloric acid gas, and the consequent interference with the regular automatic action of the generator), thus sacrificing the advantage naturally attending the use of acid of the highest degree of concentration. Upon experiment we find that acid of half-strength (sp. gr. 1·10) can be made to yield a very satisfactory proportion of chlorine. We have employed in our work potassium chlorate fused (best in platinum) and cast in sticks or broken into coarse lumps. A small Kipp's apparatus, holding about a half-litre of liquid in the two lower chambers, makes a convenient generator, and the requisite temperature may be secured by wrapping the two lower chambers with flexible metallic tubing through which steam is driven, or, with equal convenience, by simply standing the whole apparatus in heated water. When the simple precaution is taken to heat the acid to 60° or 70° C. before allowing it to come slowly into contact with the fused chlorate, no difficulty whatever is met with in the practical automatic working of the generator; but if cold acid is permitted to act upon the chlorate it becomes charged more or less with the chlorine dioxide, and a subsequent rise of temperature may cause dissociation of the explosive gas with sufficient suddenness to expel the liquid from the generator with considerable violence. The gas evolved directly from the generator is never pure chlorine. To determine the relative proportions of chlorine and chlorine dioxide (the sole products of the action according to Pebal), the gas as it issued from the generator was passed through two pipettes fitted with glass stopcocks and joined to one another. After allowing a reasonable time for the complete expulsion of air from the pipettes, the stopcocks were closed, and the pipettes were disconnected from one another and from the generator. The gas contained in one of the pipettes was slowly forced by means of carbon dioxide through a solution of potassium iodide; that in the second pipette was driven slowly by means of carbon dioxide through a hard glass tube filled with asbestos and heated to redness by a Bunsen burner, and then passed through a solution of potassium iodide. The iodine set free in each case was determined in the acidified solution by standard sodium thiosulphate, and the difference in the amounts of iodine found was attributed to the action of the oxygen of the chlorine dioxide. It was assumed that the gas filling the pipettes ranged in line was homogeneously distributed, and this assumption is probably nearly enough true for the purpose of this discussion. The temperature of the acid in the generator was determined by inserting a thermometer in the lowest chamber of the generator, so that the indication for the point of action is only approximate.

In two experiments made with acid of half strength and at indicated temperatures of 80° and 81° the chlorine in the gas amounted to 81·6 per cent and 84 per cent respectively of the mixture. A comparison experiment made with the strongest acid heated to 50°—the highest temperature attainable without evolution of the hydrochloric acid gas—the yield of chlorine was 77·3 per cent. It is evident that the acid of half strength acting at 80° is productive of a more favourable yield than the strongest acid at 50°.

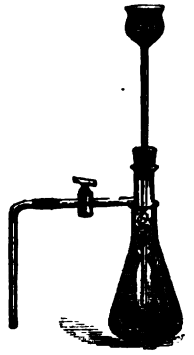
Temperatures very much higher than those employed can hardly be secured continually under the conditions of work, and yet it is plain that a considerable amount of the oxide still accompanied the chlorine. We made the attempt, therefore, to accomplish the destruction of the oxide by passing the mixed gases as they issued from the generator through a small wash bottle containing a hot saturated solution of manganous chloride in strong hydrochloric acid, making use of a device previously employed in this laboratory for the decomposition of nitric acid and chloric acid (*Am. Journ. Sci.*, xliv., 117; xlvi., 231). The results of several experiments conducted in this manner are recorded in the accompanying statement. The gas after leaving the manganous chloride passed through a small wash-bottle filled with water, was dried by calcium chloride, and collected in the pipettes arranged in train, and analysed by the method previously described.

Strength of hydrochloric acid	Temperature of acid.	Temperature of the solution of $MnCl_2$.	Bubbles of gas passing the wash-bottle per second.	Per cent of chlorine.
Sp. gr. 1·1	83°	90°	5—6	87·5
,, ,,	83	90	4—6	89·5
,, ,,	70—80	90	1—2	96·4
,, ,,	87·5	90	3	98·6
,, ,,	83	90	3	96·9

It is evident from these figures that the efficiency of the manganous chloride is considerable and naturally most manifest when the current of gas is slow. Indeed, during the passage of gas through the manganous salt small bubbles of chlorine are evolved from the entire surface of the liquid. The washed gas is pure enough for most laboratory purposes, but if chlorine perfectly free from chlorine oxide is desired it may be be obtained by passing the washed gas through a hard glass tube filled with asbestos and heated by a Bunsen flame.

In the exceptional cases in which the ignition tube is used it is well to keep in mind the fact that in starting the generator the acid should not be thrown in too great quantity upon the chlorate at first, lest an unusually large proportion of the dioxide be liberated, which may cause a slight explosion in the ignition tube. Should such be the case, however, the liquid in the wash-bottle will prevent the extension of the explosion to the gas in the generator proper, and the insertion of the wash-bottle should never be omitted when the ignition tube is to be put to use. So long as it is kept hot we have never found the apparatus other than perfectly manageable, safe, and automatic in action.

Inasmuch as a single grm. of potassium chlorate produces approximately a half-litre of chlorine, and a cubic centimetre more than a litre, it is obvious that a very compact generator may be capable of delivering a considerable supply of the gas, and we have found the diminutive apparatus shown in the accompanying figure



an exceedingly convenient addition to the furnishings of the laboratory table when chlorine is needed frequently and in small amounts. This little generator is easily made of a side-neck test-tube, funnel-tube, stopper, glass stopcock, and flask. The upper chamber of the test-tube, which is constricted near the middle, holds easily 10 grms. of the fused chlorate, and when the outer flask is filled with hot water the automatic action is satisfactory for a considerable length of time. A little wash-bottle containing a hot saturated solution of manganous chloride in strong hydrochloric acid is a desirable addition when a purer gas is needed than that delivered directly from the

generator, and the attachment of the ignition-tube makes it possible to secure the chlorine entirely free from chlorine oxide, though carrying, of course, some free oxygen.

THE DETERMINATION OF VANADIC ACID.*

By E. HINTZ and H. WEBER.

The method first indicated by Berzelius, according to which the vanadic acid is separated by a saturated solution of ammonium chloride as ammonium vanadiate, is best effected as follows, according to Ditte's proposal (*Comptes Rendus*, civ., p. 982) :—

The solution of the alkaline vanadiate must have a neutral or alkaline reaction, as in acid liquids the separation of the ammonium vanadiate is incomplete. Acid solutions, which are always more or less coloured, are therefore mixed with ammonia and heated until completely colourless. In the cold the loss of colour ensues very slowly. After the solution has cooled down to 30° or 40° pulverised ammonium chloride is gradually added, and an almost saturated solution is obtained by agitating the liquid. The use of a glass rod must here be avoided, as the ammonium vanadiate becomes firmly deposited on those parts of the sides of the beaker where they have been touched with the rod. The aqueous solution is then mixed with 4 or 5 vols. of alcohol, and allowed to stand for some hours. If the temperature of the aqueous solution when saturated with ammonium chloride does not exceed 40°, the addition of alcohol produces only a slight precipitation of this salt. The precipitate is filtered off and washed on the filter with alcohol, when any finely-divided deposit of ammonium chloride is completely removed and only unappreciable quantities of ammonium vanadiate are dissolved.

If the solution in which the vanadic acid is to be determined contains other salts sparingly soluble in alcohol, the method has to be modified. The liquid is first saturated with ammonium chloride, so that a small quantity of this salt remains undissolved, and from 4 to 5 vols. of a saturated solution of ammonium chloride are then added. After standing for some hours the supernatant liquid containing the chief part of the foreign salts is decanted through a filter; the precipitate is anew treated with saturated solution of ammonium chloride, taking care that a small quantity of the solid salt always remains undissolved. After standing for five to six hours the liquid is again decanted through the same filter, repeating the operation once or several times, as it may be needful. Lastly, the filter is perforated, and the traces of precipitate still adhering are added to the precipitate in the vessel by washing with hot water. The solution, which is now free from foreign salts, is saturated at 40° with ammonium chloride, proceeding as directed above.

The ammonium vanadiate collected upon the filter is dried, placed in a platinum crucible, the filter is added and gradually heated to redness. The vanadic acid melts, is kept for some time in a state of fusion, and is weighed when cold.

If during this operation a reduction of the vanadic acid is apprehended, the precipitate is heated to dull redness, moistened with a little nitric acid, disregarding any charred fragments of the filter which may be present, evaporated to dryness, and again heated to redness, when residues of the filter are easily burnt.

If the vanadic acid is not present in the form of alkaline salts, it must first be separated from any foreign oxides in a suitable manner and converted into an alkaline salt.

For determining vanadic acid in presence of alkaline and ammoniacal salts, A. Carnot (*Comptes Rendus*, civ., 1803) recommends it to be separated in the state of barium vanadiate. Acid solutions are first neutralised as accurately as possible with ammonia and heated to ebullition, when the yellow colour disappears. It is then precipitated with barium chloride, and the precipitate is allowed to deposit. When the precipitation is complete and the liquid has only a faint alkaline reaction, the flask is closed and rapidly cooled.

The precipitate of barium vanadiate is filtered off, washed with cold water, dried, and ignited. The precipitate has then a yellowish white colour, and its composition is represented by the formula $2BaO,V_2O_5$.

No trace of vanadic acid can be found in the filtrate from the precipitate.

Salts of strontium in slightly ammoniacal solutions containing much ammonium chloride do not precipitate the vanadic acid, whilst arsenic and phosphoric acids are under the same conditions precipitated by salts of strontium. This difference in behaviour presents, therefore, the possibility of an easy separation of vanadic acid from arsenic and phosphoric acids.

The above-mentioned reaction may also be used for separating vanadic acid from molybdic and tungstic acids, as the two latter are precipitated by strontium salts, as strontium compounds, by boiling in slightly ammoniacal solutions containing much ammonium chloride. The precipitation is, however, incomplete, and, according to Carnot, the reaction is unimportant, as molybdic and tungstic acids rarely occur in nature along with vanadic acid.

The different behaviour of vanadic acid with barium and strontium salts renders possible the following separation of barium and strontium :—

The solution of these alkaline earths is mixed with ammonium chloride and supersaturated with pure ammonia, *free from ammonium carbonate*. A dilute solution of ammonium vanadiate is added, and the mixture is boiled for some minutes, when barium vanadiate is separated as a heavy granular precipitate. It is allowed to cool with exclusion of air, filtered, and washed with cold water. In the filtrate the strontia is determined in the known manner, and for the determination of the barium the washed precipitate is dissolved in dilute hydrochloric acid, and the barium is separated as sulphate.

(To be continued).

* *Zeit. Anal. Chemie.*

THE DETERMINATION OF PHOSPHORIC ACID.

By S. W. JOHNSON.

The papers on determination of phosphorus in steel by Messrs. Dudley and Pease, by Mr. Handy, and by Messrs. Doolittle and Eavenson, remind me of some work done at my instigation in the years 1880, 1889, and 1890, and published in the Annual Reports of the Connecticut Agricultural Experiment Station for those years.

In 1880, Mr. (now Professor) H. L. Wells, demonstrated that the citrate method for determining phosphoric acid may give good results under certain conditions, but that the results are correct because of a compensation of errors, the ammonium magnesium phosphate not carrying down quite all the phosphorus, but containing enough impurities to counterbalance that loss. Over ninety determinations were made, many of them in duplicate, on forty different substances (fertilisers), after a large number of preliminary trials had indicated the effect of varying the several conditions which might influence the results. In most cases the percentages of phosphoric acid found in duplicate agreed well together, and also agreed fairly with those given by the molybdate method. In a few cases, however, considerable discrepancies appeared, and it was evident that further study was needful before the citrate method could be fully trusted for fertiliser work.

In 1889, in conjunction with Dr. T. B. Osborne, investigation of the citrate method was resumed. The German agricultural chemists were beginning to use it, and J. H. Vogel had published details of procedure. We found that Vogel's process gave results too low, and not closely agreeing with the molybdate method. By using more and stronger magnesium mixture and a larger quantity of concentrated ammonia, we overcame this discrepancy, and in sixty-seven determinations on bone-dust superphosphates, cotton-hull ashes, cotton-seed meal, tankage, bone char, phosphatic guano, and phosphate rock, we found that but three citrate determinations differed from those by molybdate by more than 0·3 per cent, and but four others by more than 0·2 per cent. The greatest discrepancy between the two methods was 0·41 per cent. while the average difference was 0·09 per cent. In thirty cases the citrate method averaged 0·117 per cent more, in thirty-three cases 0·079 per cent less, than the molybdate method. These percentages were reckoned on 0·4 grm. of substance containing from 0·5 to 31·5 per cent of P_2O_5. The determinations were not made with unusual care, but were turned off rapidly as a part of the routine work of the Station.

The citrate method was found to give unsatisfactory results where iron and alumina were present in considerable quantity, as in case of "Grand Cayman's Rock," "Thomas Gilchrist Slag," and "Keystone Phosphate." A series of trials under varied conditions was made in 1889, with the hope to ascertain the cause of the discrepancies, but without success.

Some analyses of the ignited precipitate obtained by the citrate method may be quoted here :—

Composition of Ignited "Citrate Precipitates."

	Bone.	Superphosphate.	Grand Cayman's Phosphate.	South Carolina Rock.	Bolivian Guano.	Dissolved Bone-black.
Carbon—	0·41	0·19	0·44	0·15	0·48	0·27
Silica—	—	0·12	0·40	0·10	0·24	0·19
Calcium oxide—	2·59	2·13	2·05	3·21	3·95	2·05
Magnesium pyrophosphate—	95·49	96·07	95·66	95·77	94·98	97·83
Ferric and aluminum phosphate—	—	—	0·71	0·35	—	0·31
Loss—	1·51	1·49	0·74	0·42	0·35	—
	100·00	100·00	100·00	100·00	100·00	100·65

The loss probably consisted in part of magnesia, and in part also of pyrophosphoric acid. It is seen that the ignited precipitates contained from 2 to 4 per cent of lime, that iron and alumina entered into the precipitate in small quantity when these elements were abundant in the original substance, and that where there was little or no loss the recovered phosphoric acid amounted to from 95 to 97·8 per cent of the precipitate.

In case of Grand Cayman's phosphate rock, duplicate determinations differed as much as 0·3 per cent, and the variations of duplicates of Thomas slag and Keystone phosphate were even greater. It was also found that by changing the proportions of the reagents, and by using on the one hand moderate, and on the other vigorous and prolonged, agitation, the quantity of phosphoric acid, reckoned from the ignited precipitate, fluctuated, in case of Thomas slag and Keystone phosphate, 2½ and 3½ per cent respectively, although by using large quantities of magnesia mixture and of strong ammonia, accordant and high results were realised.

Thus far we employed the modified rapid molybdate method, precipitating from hot solutions and digesting for one hour at 65° C. Finally, in 1890, we found that under this procedure the molybdate method, though satisfactory in absence of ferric, aluminum, and manganese salts, is, in their presence, little better than the citrate method. In case of Keystone phosphate three determinations by Osborne, using the U.S. "official" method, gave figures ranging from 45·25 to 46·68 per cent!

It was therefore necessary to return to the original Sonnenschein method, and make the precipitations at 40° to 50° C., during six hours. Six determinations thus carried out by Osborne, gave results from 44·67 to 44·86, the average being 44·82 per cent.

Comparative duplicate trials on a carefully made up solution of known composition with $P_2O_5 = 18·93$ per cent* (from crystallised sodium phosphate), $Fe_2O_3 = 20$ per cent, $Al_2O_3 = 4·72$ per cent, and $MnO = 5·09$ per cent (from sulphates), yielded Osborne, by the original Sonnenschein method, 18·92 and 18·94 per cent, and by the "official" method 19·26 and 19·26 per cent!

We proved that with relative excess of nitric acid, or relative deficiency of molybdic acid, a portion of phosphoric acid may easily fail to be thrown down. We also found that when precipitation is made hot and digestion is conducted at 65° C., ferric iron, and aluminum, if present, are to some extent included in the yellow precipitate, and, when this is dissolved in the subsequent treatment with ammonia, they pass into the alkaline solution, and thence into the ammonium-magnesium phosphate.

To sum up, the citrate method only gives good results by compensation of its errors, and under exactly defined conditions which must be empirically determined. A procedure good for calcium phosphates is quite inapplicable to ferric and aluminum phosphates.

Again, the molybdic method, when carried out rapidly at temperatures higher than 50°, or as high as 65° C., in presence of trivalent iron, aluminum, or manganese, gives results too high, and in presence of great excess of nitric acid may give results too low, unless the filtrates from the yellow precipitate are mixed with additional molybdic solution and further digested until no more precipitate can be thrown down.—*Journal of the American Chemical Society*, vol. xvi., No. 7.

THE PHYSICAL SOCIETY OF LONDON.

The following Circular has been issued to the Members of this Society:—

The Physical Society has for many years met, by permission of the Lords of the Committee of the Council on Education, in the Royal College of Science at South Kensington. The Council, after careful consideration, have come to the conclusion that the meetings of the Society would be more accessible to the majority of the Members if they were held in some more central situation; and that this advantage would more than compensate for the loss of others which the Society has unquestionably received from the long-continued hospitality of the Department of Science and Art.

The meetings of the Physical Society will therefore henceforward be held on the same day and at the same hour as heretofore, but, by the kind permission of the Council of the Chemical Society, in the rooms of that Society in Burlington House.

All communications to the Secretaries or other Officers of the Society may in future be addressed to Burlington House, or to the Secretaries at their respective addresses as given in the List of Members of the Society.

The Council have also decided to initiate the publication of a series of Abstracts of Papers on Physics. The slender resources at their command make it necessary to begin cautiously. At first abstracts will only be given of papers which appear in a certain number of the more important Foreign Magazines. They will be published

* Determined in the usual manner as magnesium pyrophosphate.

regularly at the beginning of each month in the form of a Supplement to the Proceedings of the Society. The first number will be issued in January, 1895. Should the scheme prove successful, it is intended to enlarge its scope.

The Abstracts will for a time be edited by Mr. Swinburne.

It has also been decided to make a new departure of a somewhat novel kind. For some time past printed copies of the more important papers have been circulated before the meetings among Members who are likely to take part in the discussion on them. It has thus been proved that previous knowledge of the contents of a paper promotes, instead of detracting from, the interest with which the author's account of his work is heard and commented on by the Society at its meetings. But the Council feel that cases may arise in which the author may wish that his paper should be published as soon as possible. They have therefore decided that, if an author so desires, and if such a course appears desirable, they will take steps to ensure that the publication of a paper is not in any way delayed in order that it may be read before publication, and that they will if necessary postpone the reading and discussion of a paper until after it has been published.

In making this announcement the Council believe that the ordinary procedure of the Society with regard to reading and publication will be much the same as heretofore, but they wish it to be understood that they are willing to deal with special cases in an exceptional way.

It will be obvious from the above that the Council of the Physical Society is about to undertake some serious financial responsibilities in the hope of promoting the advance of Physical Science. They trust that Members of the Society will assist them in this effort, especially by drawing the attention of those Physicists who are not already Members to the work and objects of the Society.

—We are, dear Sir, your obedient Servants,

T. H. Blakesley, Harry M. Elder, } *Hon. Secs.*

NOTICES OF BOOKS.

An Introduction to the Study of Metallurgy. By W. C. Roberts-Austen, C.B., F.R.S. Third Edition, Revised and Enlarged. One of a Series of Treatises written by Associates of the Royal School of Mines. London: Charles Griffin and Co. 1894.

The study of the science of Metallurgy is of great antiquity, and the literature of the subject is most voluminous; in most, or perhaps all, English works on metallurgy each metal is dealt with separately, but in this work the author has endeavoured to treat the subject as a whole, not taking any individual metal and minutely describing the methods of working it, but rather choosing typical methods applicable to, and used in connection with, groups of metals. This, the third, edition has, we find, been enlarged by a hundred pages, and new chapters have been added on Thermo-chemistry and the Microstructure of Metals and Alloys. These are both important subjects, and have of late years been attracting more and more attention.

After an introductory chapter on "The Relation of Metallurgy to Chemistry," in which the author gives an historical sketch of the subject from the earliest times onwards, we come to the physical properties of metals, dealing with molecular structure, malleability, brittleness, strength, &c.. The influence of the presence, even in minute quantities, of foreign materials on any metal is well known, that of carbon on iron being specially notable; while another interesting example is the enormous increase of strength attained by the addition of aluminium to copper, aluminium-bronze being the strongest of all the copper alloys. The "flow" of metals is also here considered, and it is pointed out that the strength of steel can be greatly increased by previously subjecting it to an enormous pressure in the direction of the intended stress. Sir Benjamin Baker, writing of the Forth Bridge, says, "At least one-half of the 42,000 tons of steel in the Forth Bridge is in compression, and the same proportion holds good in most bridges, so the importance of gaining an increased resistance of 60 per cent without any sacrifice in the facility of working, and safety, belonging to a highly ductile material, can hardly be exaggerated."

Chapter III. deals with alloys, and the various manners in which metals may be united, either by fusion, by pressure, or by electro-deposition, together with their properties, colour, &c.

Chapter V. deals at considerable length with Fuel and and Thermal Measurements. Fuels are divided into two principal classes, natural and prepared; to the first class belong wood, turf, coal, and such like; while the second class comprises compressed fuels, coke, charcoal, and liquid or gaseous fuels. The value of all these depends on the quantity of hydrogen and carbon they contain; the amount of ash in a solid fuel is also a point of considerable importance.

Pyrometry and pyrometers next come in for a good share of attention, all the latest developments being thoroughly considered.

In the chapter on materials and products of metallurgical processes, the general principles of reduction, fusion, slagging, &c., are set forth, but—as has been before mentioned—no individual process or metal is singled out for special mention. The next chapter, however, on furnaces, departs somewhat from that rule, many individual hearths and furnaces being minutely described and illustrated. The electric furnace, originally devised by the late Sir Wm. Siemens, is rather lightly passed over, though the author expresses his opinion that it will probably become a powerful instrument of research in the near future; in view of its growing importance, we hope to hear more of it in a subsequent edition.

Chapter X., on Typical Metallurgical Processes, is of extreme interest. All processes are divided into wet and dry, while these are again subdivided in several manners, such as simple fusion with fluxes, reduction by carbonic oxide; concentration as sulphide, arsenide, or in another metal; solution in acids, roasting and leaching, chlorination, &c. Each of these processes is taken *seriatim* and fully described; there are also some interesting tables, showing graphically the relation and order of each step in the various methods.

In the final chapter, on Economic Considerations, the author writes strongly, and we think with good reason, on the present abominable methods of the Trades'-Union leaders; under the guise of liberty they are really practising tyranny of the most oppressive kind; but so long as the men are blind to their own and (what is the same thing) their masters' interests, and listen only to the professional agitator, whose real aim is only notoriety for himself, so long will strikes occur, trade leave the country, and thus more and more men be thrown out of work. Great Britain will not be the first empire whose downfall has been brought about by mob government, and we are afraid it will not be the last.

Electro-Chemical Analysis. By Edgar F. Smith, Professor of Chemistry, University of Pennsylvania. Second Edition, Revised and Enlarged. Philadelphia: P. Blakiston, Son, and Co. 1894.

There is no doubt that, in a large number of cases, the electrolytic estimation of metals is—owing to its cleanliness, accuracy, and rapidity—far preferable to the older and more tedious methods of gravimetric analysis. Prof. Smith complains that the larger text-books devoted to analysis have omitted electrolysis from their pages, thus

rendering its special treatment necessary and desirable. That is happily no longer the case; the last edition of "Select Methods in Chemical Analysis," by William Crookes, F.R.S. (published by Longmans and Co.), goes very thoroughly into the subject. We note that emphasis is herein laid on the desirability of reporting that results have been obtained by a current of definite density, rather than by one yielding so many cubic centimetres of electrolytic gas per minute. We quite agree with the author that there is much to be said in favour of this recommendation. A current of 1 ampère equals 10·436 c.c. of oxy-hydrogen gas per minute, or 19·69 m.grms. of metallic copper, or 67·1 m.grms. of silver, per minute. Results given with reference to ampères or decimal parts thereof are assuredly more easy of comprehension than those given in c.c. of gas.

The sources of electrical energy may be briefly stated as, primary batteries, dynamo and magneto machines, and storage batteries or accumulators: of these we prefer the latter; the current is more constant, and this class of battery gives less trouble than any other. It may, of course, often happen that an accumulator cannot be used on account of there being no facilities available for re-charging; in this case a bichromate battery will be found very convenient. The Leclanché cell is not of much use in this work, as the E.M.F. decreases so rapidly when a continuous flow of current is being used. By means of rheostats (several of which are described and illustrated) the strength of the current can be controlled with great accuracy. For measuring the currents used we do not favour the voltameter, though it is here said to be "the simplest and most convenient." Mechanical voltameters and ammeters for this purpose are now made so accurately that fractions of either unit can be easily read without any trouble beyond that of pressing a key.

The first part of this book ends with a very interesting historical sketch of the inception and growth of electrolytic analysis. Gaultier de Claubry is credited with being the first to apply the electric current to the detection of metals in solution, in the year 1850, and, though many other workers have been constantly improving and adding to our knowledge, it is to the activity of the Aachen school, as represented by Classen and v. Reiss, that electrolysis owes the importance it now possesses in the eyes of the chemical public. The details of the more important methods devised by Classen and his fellow-workers are all mentioned under the headings of the respective metals to which they are applied.

The second or special part of this excellent work is devoted to the separation and estimation of the various metals of common occurrence, each metal being taken in turn, all details of manipulation and apparatus being fully described and plentifully illustrated.

An important and useful feature of this book is a list of the literature bearing on the particular subject, preceding the description of every process mentioned, thus enabling students, with very little trouble, to refer to the original articles and communications, should they wish it.

In conclusion, we may add that it has not been considered necessary to include an outline of the electrolysis of minerals or alloys, believing that the experience gained in the analyses already described will enable the analyst to map out the proper course to be pursued as occasion arises.

Notes on Polarised Light, for Students of Mineralogy. By A. E. Munby, B.A., F.C.S. Newcastle-on-Tyne: Andrew Reid, Sons, and Co. 1894.

These notes have been prepared for the purpose of giving to students of mineralogy beginning polariscope work some explanation of the optical phenomena observed, and of the terms used in the classification of crystalline substances, according to their optical symmetry. The author describes very clearly the construction and use of the Nicol prism, and the polariscope, of which they form the essential part; after which he gives details of the various experiments to be carried on with this instrument, and explains the results arrived at. The different behaviour of various crystals is pointed out, the distinction between positive and negative crystals being very clearly shown.

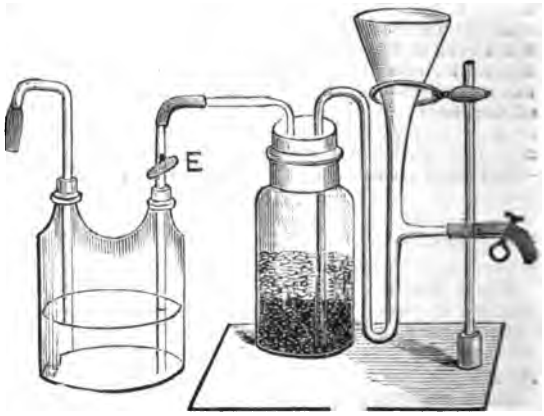
Those students who have little or no knowledge of mathematics or higher optics will no doubt find these few pages of considerable value. Two plates of figures add greatly to the lucidity of the text.

CORRESPONDENCE.

A NEW SULPHURETTED HYDROGEN APPARATUS.

To the Editor of the Chemical News.

Sir,—In your issue for August 24th (Chem. News, vol. lxx., p. 95) is described a new form of H_2S apparatus. It is no easy matter to fit the cork in such a way that there shall be no leak, under the great pressure caused by the rising of the acid in the funnel when the tap, E, of the wash-bottle is shut off. The following modification obviates this difficulty, and enables much slighter variations in



the pressure of gas, within the generating bottle, to force out the acid, although a sufficient working pressure is maintained.

No further explanation is necessary.—I am, &c.,

H. Brearley.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxix., No. 10, September 3, 1894.

Assimilability of Potassa in Poor, Siliceous Soils by the Action of Nitrates.—P. Pichard.—Potassa which is in general sparingly assimilable, such as is found in siliceous rocks, in sandstones, and in sands, can suffice for the demands of plants which are exacting in this respect, by means of a suitable nitrification maintained in these soils, or by the addition of chemical nitrates. Nitric nitrogen is the excitant and the chief factor of all vegetation.

New Gravimetric Determination of Glucose.—Fernand Gaud.—In a porcelain capsule the author mixes 50 c.c. of cupro-potassic liquid, prepared at the very moment, and 50 c.c. of water. After boiling for two or three minutes it is set upon a boiling water-bath, and 25 c.c. of the saccharine liquid (made up to 1 per cent) is added at once. After 10 minutes the reduction is complete, the blue liquid is decanted, and the precipitate is washed with boiled distilled water. When the washings are neutral to phenolphthalein the precipitate is washed into a specific gravity bottle holding from 20 to 25 c.c. Its capacity at 0° must be known beforehand. The level is made up with boiling water and the bottle is weighed. Let P be the weight of the liquid and the precipitate, the total volume of which is equal to the capacity of the bottle at the temperature, t, of the experiment, *i.e.*, $v_t = v_0[1+3\beta(t-t_0)]$. Knowing also the specific gravity $\Delta = 5{\cdot}881$ of dried cuprous oxide, and d the specific gravity (found in the tables) of water at the temperature of the experiment, t, we find the weight, p, of the precipitate by the formula—

$$p = \frac{P - V_t\, d}{1 - \frac{d}{\Delta}}$$

Consecutive Phenomena in the Dialysis of the Cells of Beer Yeast.—F. Onimus.—The author seeks to ascertain whether it is the immediate contact of beer-yeast or the products of its secretion which effect the phenomena of fermentation. His experiments show that beer-yeast certainly secretes a dialysable substance, and that the inversion of the sugar takes place before the new cells appear.

No. 11, September 10, 1894.

This issue contains no chemical matter.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. xi.-xii., No. 13.

Novel Muffle Furnaces.—Emile Aubin.—The construction of these muffle furnaces cannot be explained without the accompanying figures. As compared with ordinary gas muffle-furnaces they are said to effect a great economy of time and of gas.

On the Emetics.—Paul Adam.—Boric, arsenious, and antimonious acids react upon the acids of the acid alcohols. For the lactate and the salicylate the formation of the ether is evident. The case of ordinary tartar emetic is less simple, because we cannot isolate the neutral antimonio-tartrate, but the analogies and the reactions must lead us to consider substances of this kind not as double salts, but as ether salts.

Melting- and Boiling-points of some Phenols, and of their Benzoic Ethers.—A. Béhal and E. Choay.—The authors give their results in the form of tables. The benzoates are all solid except that of orthocresol, which is liquid. They crystallise well and distil at the ordinary pressure, without any trace of decomposition. They are insoluble in water, but soluble in most of the organic solvents.

Compounds of Pyridin with the Permanganates.—T. Klobb.—Ammonia and pyridin give two parallel series of derivatives. The parallelism is traced in the compounds of silver, copper, cadmium, zinc, and nickel.

On Certain Derivatives of Campholic Acid.—M. Guerbet.—This paper is not adapted for useful abstraction.

Experiments on Coal Immersed in Water.—G. Arth.—The author finds that for coal reduced into small fragments and immersed in water the variation of the composition of the organic matter is very slight whether the water flows or is at rest. In practice the modifications may be considered as negligible for a duration of twelve months. The differences may become more important if the time is further prolonged or if the material is more comminuted. The action of air is more decided than that of water, but it is unimportant if the coal is placed in conditions such that it does not heat. The modifications observed do not ensue in the same manner in water and in air, nor are they alike in all kinds of coal.

Chemical Composition of the Colostrum of the Cow.—L. Naudin.—The proportions of extract of lactose and of butter present nothing remarkable. The ash and the proteïc matter undergo simultaneously very important changes. The mineral matter is in much larger quantity than in normal milk; the insoluble ash, especially the calcium phosphate, is increased. Contrary to what we observe in normal milk, the serum obtained with the colostrum holds sulphates in solution. They may reach from 45 to 60 centigrms. per litre, and decrease gradually until the milk becomes normal.

Universal Gas-Volumeter of Dr. G. Lunge.—An abstract of this paper would require the eleven accompanying figures.

Disinfection by Electricity, a Study on the Hermite Process of A. A. Lambert.—We shall endeavour to notice this process at some length.

MISCELLANEOUS.

Schools of Chemistry, &c.—The following additional information is appended to that which appeared in the STUDENT'S NUMBER:—

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Medical Education in the United States.—According to the *Lancet Clinic*, an American professional organ (quoted in the *Medical Press*), "In Ohio any five men can organise and obtain a legal college charter, and with it in six weeks, or six days, can grant a legal diploma." (!)

Chemico-Technical Study in England.—The *Chemiker Zeitung* observes that in certain English establishments for higher education, the question of chemico-technical instruction seems to be receding rather than advancing. Thus at University College, London, the separate Chair of Chemical Technology has been given up. All the arguments and warnings of authorities, such as Stanford and Watson Smith, seem to yield little fruit.

On a Reaction of the Aldehyds; Differentiation of the Aldoses and the Ketoses.—A. Villiers and M. Fayolle.—The authors have made use of a very sensitive reagent (aqueous solution of magenta decolourised by means of sulphurous acid), *i.e.*, prepared without excess of sulphurous acid. They consider that every urine containing acetone must produce the re-colouration of the magenta. The use of the solution of magenta decolourised with sulphurous acid enables us to verify the purity of acetone. The same reagent serves to differentiate the aldosic from the ketosic sugars. Glucose, invert-sugar, and galactose redden the reagent as well as the aldehyds; it is the same with the reductive dextrines. Two samples of pure levulose and sorbine give a completely negative result.—*Bull. Soc. Chim. de Paris*, xi.-xii., No. 14.

The Zurich Exhibition.—According to the *Chemiker Zeitung* the distribution of prizes at this Exhibition has been over-liberal. Of the 1300 exhibitors no fewer than 1199 have received prizes. In the department of Chemical Industry the three highest distinctions have been awarded to the manure-works, Grüze; the gelatin-works—both of Wintherthur; and the soap-works of Steinfels, of Zurich. The Cantonal chemist of the Pays du Vaud (F. Sciler) notices that the minimum limit of fat in milk in that district (3 per cent) is too low, as it allows of the removal of a portion of the cream. An examination of meat, which had occasioned eighty attacks of sickness and two deaths, led to the detection of an extremely pathogenic bacterium, not previously described.

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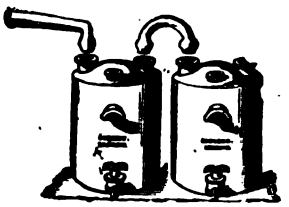

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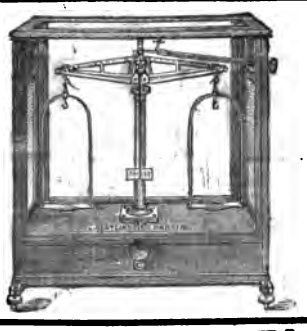

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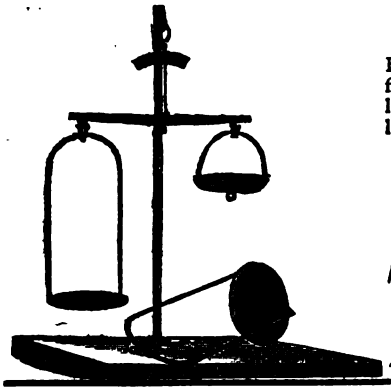

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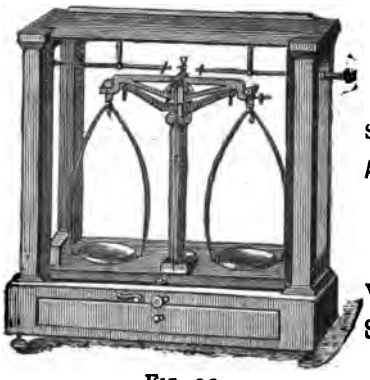

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THE ACTION OF REDUCING AGENTS ON IODIC ACID.*

By CHARLOTTE F. ROBERTS.

I. *The Absorption of Nitric Oxide by Iodic Acid.*

The following investigations were first undertaken with the object of studying the solubility of nitric oxide in iodic acid. Although most chemical authorities agree in the statement that nitric oxide is absorbed by iodic acid with the separation of iodine, there is a certain indefiniteness with regard to the *degree* of solubility, which led me to investigate the subject for myself. Thus, Gmelin-Kraut states that "All the lower oxides of nitrogen decompose iodic acid into iodine and nitric acid, but the decomposition takes place only in presence of a considerable quantity of water," but the *degree of ease* with which the decomposition takes place meets with no comment, and the "considerable quantity of water" seems a somewhat indefinite condition. Kämmerer,† who is the authority referred to for the above facts, and who, some years ago, made a thorough study of iodic acid, says, without referring to any illustrative experiments, "At ordinary temperature, I_2O_5 is reduced only in aqueous solution by nitric oxide, but this gas is without action upon the water-free acid and its solution in concentrated sulphuric acid. At 100° the latter is very slowly, the water-free acid not at all decomposed."

A portion of this latter statement was very easily verified. Some nitric oxide was passed through the dry acid, and other portions were collected and allowed to stand over sulphuric acid solutions of HIO_3 and I_2O_5, without any appreciable separation of iodine.

In order to test the solubility of the gas in *aqueous* solutions of iodic acid, the nitric oxide was prepared in a generator containing potassium nitrate and ferrous sulphate, the air having been previously driven from the apparatus by means of carbon dioxide. The gas was next passed into a Will and Varrentrapp tube containing potassium iodide, and then into a Geissler bulb containing the iodic acid. The experiment was made several times with iodic acid of various degrees of concentration, and always with the same result. There was no evidence of iodine being set free from the iodic acid, though the liquid showed occasionally a barely perceptible tinge of yellow. There was, however, a smaller amount of nitric oxide collected by two or three cubic centimetres than should have resulted from the amount of nitrate used, and on two or three occasions, an odour like that of chlorine was observed about the Geissler bulb, when the apparatus was disconnected, which could only be explained on the supposition that gaseous hydrochloric acid was carried over from the generator through the potassium iodide.

A later experiment in which nitric oxide was collected in a tube containing iodic acid and hydrochloric acid so dilute that no reaction took place between the two acids in the cold, showed that under these circumstances the nitric oxide was absorbed without any separation of iodine and that the liquid became yellow and gave odour like that of chlorine, so that the above seemed a plausible explanation of the disappearance of some nitric oxide in the Geissler bulb without a simultaneous liberation of iodine.

Two or three experiments were then made with the apparatus as before, but with the addition of a new absorption tube containing silver nitrate to prevent the hydrochloric acid from going over into the iodic acid. Still there was no evidence of iodine being set free. It seemed apparent, then, that the nitric oxide was not sufficiently soluble in iodic acid, so that it could be absorbed by simply passing it rapidly through the solution.

To determine whether the gas was soluble upon long contact with the iodic acid or not, different portions were collected in U-tubes closed at one end and filled with solutions of iodic acid of different degrees of concentration. The gas had been collected and allowed to stand over potassium iodide and sodium hydroxide for from twenty-four to forty-eight hours before being transferred to the U-tube, in order to remove completely any other oxide of nitrogen which might be present. Solutions of iodic acid were used in the different U-tubes varying from a saturated solution containing about 50 grms. to 25 cubic centimetres to a rather dilute solution containing not more than 5 grms. to 25 cubic centimetres. There was no apparent absorption as the gas passed up through the liquid, but after the nitric oxide had been standing over the iodic acid for a few moments, iodine appeared on the surface of the liquid. This deposit gradually increased in amount and the liquid rose in the tube, reaching its maximum in 24 hours or less, depending on the amount of gas used.

The result of my experiments, then, has been to show that nitric oxide is absorbed by solutions of iodic acid of any degree of strength, but the reaction takes place slowly even when the gas is confined over the acid, and not at all when passed rapidly through the solution.

II. *The Action of Reducing Agents on Iodic Acid in presence of Hydrochloric Acid.*

It has already been stated that when the nitric oxide was collected over iodic acid mixed with dilute hydrochloric acid, the gas was absorbed, but there was no liberation of iodine, and in some cases an odour like that of chlorine was observed when the tube was opened. A similar phenomenon was noticed with several other reducing agents. It is well known that iodic acid with *strong* hydrochloric acid, or *heated* with dilute hydrochloric acid, forms iodine chloride and may set free chlorine, but in these experiments the dilute acids were used in the cold, and there was no change apparent until the reducing agent was added. Besides the nitric oxide, other substances which had a similar effect were potassium iodide, sodium thiosulphate, arsenious oxide, ferrous sulphate, stannous chloride, and potassium sulphocyanide. If the reducing agent was added in a very concentrated form, iodine was sometimes evolved, and in many cases traces of iodine would first form where the reagent touched the liquid, but would disappear on shaking, and a light yellow liquid would result with an odour like that of chlorine.

The first explanation of this phenomenon that suggested itself was that the iodic acid was not immediately completely deoxidised by the reducing agent, but was first transformed to a lower oxide of iodine (Gmelin-Kraut, *Anorg. Chemie*, i., 2, 290) which was more active and therefore more easily acted upon by hydrochloric acid than the iodic acid itself, and that the chlorine thus set free united wholly or partially with the iodine formed by the first reduction. It was with the object of studying the reduction of iodic acid in the presence of hydrochloric acid that some experiments were undertaken with potassium iodide, iodic acid, and dilute hydrochloric acid. Potassium iodide was chosen as the reducing agent on account of the simplicity of its oxidation products. Approximately N/10 solutions of iodic acid and potassium iodide were used and dilute hydrochloric acid of specific gravity 1·05. The latter acid was so dilute that it could be added in apparently indefinite quantities to the iodic acid without producing any perceptible odour or change of colour.

* Contributions from the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, xlviii., August, 1894.

† *Journ. f. Prakt. Chem.*, lxxxiii., 73.

With 10 c.c. of iodic acid and half that volume of hydrochloric acid, if the potassium iodide was added gradually from a burette, the addition of 4 or 5 c.c. gave a clear, light yellow liquid in which no free iodine could be proved either by starch or chloroform. As the amount of potassium iodide increases, the liquid gradually becomes orange until, finally, particles of iodine are precipitated out and accumulate until they reach the quantitative yield represented by the common equation—

$$5KI+HIO_3+5HCl=3H_2O+5KCl+3I_2.$$

These phenomena seem to indicate that the reaction takes place in two steps, giving first the iodine chloride, and then the decomposition of this by means of more potassium iodide, setting free iodine. Even after solid particles of iodine appear in the liquid, starch paste is not coloured blue, showing the well-known disturbing action of the chloride of iodine. That the intermediate product is essentially the *monochloride* of iodine instead of the *trichloride* may be inferred from the superior stability of the former in dilute solutions containing hydrochloric acid, since most authorities agree that the trichloride is completely broken up in dilute solutions into the monochloride, iodic acid, and hydrochloric acid. If any trichloride were first formed and underwent this decomposition, the final form of the reaction would be the same as if the monochloride were the sole product. This inference was further confirmed by later results and by the following experiment:—

The clear yellow liquid obtained by putting together 10 c.c. of iodic acid, half that volume of hydrochloric acid, and 4 c.c. of potassium iodide was agitated with benzene, which is said to dissolve iodine trichloride with a dark cherry-red colour (Ladenburg, "Handwörterbuch," v., 359). The result was a barely perceptible pinkish tinge to the benzene, which left no appreciable residue on evaporation. After separating the benzene and adding ether, the colour was quickly taken from the aqueous solution, and the ether became yellow, and, on evaporation, left a considerable quantity of a volatile reddish brown liquid. This experiment showed plainly that the essential product was iodine monochloride.

In three different ways I have tried to estimate the proportions in which iodic acid and potassium iodide unite in presence of an excess of the former and hydrochloric acid. The direct method of letting potassium iodide of known strength slowly into a mixture of the two acids and determining the first appearance of free iodine is difficult on account of the action of the iodine chloride on the blue iodide of starch which one would naturally use as an indicator. I have succeeded, however, in getting an approximate result, by taking out a drop of the liquid from time to time and testing on starch paper. With 5 c.c. of iodic acid, 9·5 c.c. of potassium iodide were added before there was any effect on the starch paper. This would indicate molecular proportions of iodic acid to potassium iodide as 1 : 1·9.

In the second method, 20 c.c. of iodic acid, 10 of hydrochloric acid, and 4 of potassium iodide were put together; the resulting iodine chloride was extracted with ether and separated with a separating funnel. The aqueous solution containing free hydrochloric acid was then treated with an excess of potassium iodide, and the amount of iodine set free determined, after neutralisation, by alkaline arsenious acid. From this the iodic acid remaining in the solution after the extraction of the iodine chloride could be readily estimated, and the difference between this and the amount taken gave the amount used in the reaction. Three trials of this experiment gave the following results for the molecular proportions in which the iodic acid and potassium iodide unite in presence of hydrochloric acid while the iodic acid is in excess:—

HIO_3 : KI
1 : 2·06
1 : 1·99
1 : 1·9
} Average = 1 : 1·98.

The third method consisted in putting together the reagents in the same proportion as above and then decomposing the iodine chloride with acid potassium carbonate and estimating the iodine set free by alkaline arsenious acid. According to Gay-Lussac, the reaction between iodine chloride and an alkali is represented thus—

$$6KOH+5ICl=5KCl+KIO_3+3H_2O+2I_2.$$

The iodine shown by the arsenious acid is then only four-fifths of that in the iodine chloride. Making this correction and knowing the amount of iodine in the potassium iodide used, it becomes an easy matter to determine the iodic acid which has contributed to the formation of the iodine chloride.

The following results were obtained:—

HIO_3 : KI
1 : 1·92
1 : 2·02
} Average = 1 : 1·97.

The three methods, then, agree fairly well in indicating two molecules of potassium iodide to one of iodic acid, a reaction which would be expressed by the following equation:—

$$HIO_3+2KI+5HCl=3H_2O+2KCl+3ICl.$$

The formation of iodine monochloride has thus been proved by three methods, two of which would be sufficient to establish the reaction. The first two methods are independent of the reaction between iodine monochloride and carbonated alkalis, while the third depends directly upon that reaction. Assuming the correctness of Gay-Lussac's equation, this third method may be taken simply as an additional way of proving what has been already sufficiently established in two different ways. On the other hand, considering the formation of iodine chloride sufficiently established by the two other methods, the last set of experiments may be used to discriminate between Gay-Lussac's and Grüneberg's reaction. The latter (*Journ. für Prakt. Chemie*, lx., 172) states, without describing his work in detail, that he has found by many carefully repeated experiments that the action of alkaline carbonates on iodine monochloride gives potassium chloride and potassium chlorate, and *all* of the iodine is set free. My results, however, show the correctness of Gay-Lussac's equation, since it is only on the assumption that *four-fifths* of the iodine is set free that my third method of work gives results corresponding with those obtained in two other ways. Moreover, some iodine chloride was prepared by putting together potassium iodide, and an excess of iodic and hydrochloric acids, and extracting with ether, specially purified by standing over sodium bisulphite and distilling from sodium hydroxide. Portions of this ethereal solution were drawn off from a burette and treated with potassium iodide, and the iodine estimated by sodium thiosulphate. Similar portions were then treated with hydrogen potassium carbonate, and the iodine estimated by arsenious acid. Grüneberg's reaction would demand that one-half as much iodine should be set free in the latter case as in the former, instead of which only four-fifths of that amount was found, which is in direct agreement with Gay-Lussac's equation.

III. *Action of Iodine on Iodic Acid in presence of Hydrochloric Acid.*

Some light is thrown upon the reaction just established by the behaviour of free iodine in a mixture of iodic and hydrochloric acids.

Although a solution of iodine in iodic acid turns starch blue, and also one of iodine in hydrochloric acid, if the solutions be mixed, the starch immediately loses its colour, but regains it on the addition of alkaline carbonate. Also, if a colourless mixture of iodic and hydrochloric acids be taken, and aqueous iodine added gradually from a burette, the first effect of the addition is to make a colourless liquid in which the presence of iodine can be proved only upon addition of an alkaline carbonate.

Further addition of the iodine gives a yellow liquid whose properties and reactions seem identical with that obtained by putting together iodic and hydrochloric acids and potassium iodide. This same liquid may be produced by allowing iodine to dissolve slowly in the cold in a mixture of dilute hydrochloric and iodic acids.

Apparently, then, the action of reducing agents is to set free iodine from the iodic acid, and this dissolves in a mixture of iodic and hydrochloric acids to form iodine chloride. Two experiments were made to determine the proportions in which the iodine and iodic acid unite in this reaction. Solid iodine, in carefully weighed quantity, was allowed to dissolve in a mixture of the acids, then the acid was neutralised with alkaline carbonate, and the iodine set free estimated by means of arsenious acid. The molecular proportions of iodic acid to iodine as found were as follows :—

HIO_3 : I
1 : 4·02
1 : 4·07

The same proportions were obtained by direct titration of iodic acid against a solution of iodine in hydrochloric acid of known strength. The operation was performed in a flask, a definite quantity of iodic acid being first introduced and then the solution of iodine added from a burette until, upon shaking the flask, the presence of free iodine was indicated by the characteristic colour given to chloroform.

The molecular proportions found were—

HIO_3 : I
1 : 4·02
1 : 4·06

These results, it will be seen, are in complete accordance with those obtained by the former method, and indicate the following reaction :—

$$HIO_3+2I_2+5HCl=3H_2O+5ICl.$$

The equation obtained above for the reaction between iodic acid, potassium iodide, and hydrochloric acid, viz.,—

$$HIO_3+2KI+5HCl=3H_2O+2KCl+3ICl,$$

can be derived directly by a combination of the ordinary equation, in which the iodine is set free,—

$$[5KI+HIO_3+5HCl=3H_2O+5KCl+3I_2]2,$$

with the equation just established,—

$$[HIO_3+2I_2+5HCl=3H_2O+5ICl]3,$$

in which the iodine reacts upon iodic acid. This fact supports the assumption that the effect of a reducing agent upon an excess of iodic acid in presence of hydrochloric acid is to set free iodine, which then dissolves in a mixture of the two acids to form iodine monochloride.

Iodine has apparently no effect upon either acid taken singly, and there is nothing in these experiments to show whether the action of the iodine on the iodic acid in the mixture of the two acids is in the first instance of an oxidising or reducing nature. It may be that the iodic acid is first reduced to a lower oxide, as has been previously suggested, or that it is oxidised to periodic acid. The first condition is expressed in equations I., and the latter in equations II., from which it is seen that either assumption agrees with the equations just established.

I.
$2HIO_3+I_2+2HCl=I_4O_4+2H_2O+2ICl$
$I_2O_4+3I_2+8HCl=4H_2O+8ICl$
Combined: $2HIO_3+4I_2+10HCl=10ICl+6H_2O$

II.
$2HIO_3+2H_2O+2I_2=4HI+H_2O+I_2O_7$
$I_2O_7+4HI+10HCl=7H_2O+6ICl+2Cl_2$
$2Cl_2+2I_2=4ICl$
Combined: $2HIO_3+4I_2+10HCl=10ICl+6H_2O$

In any case it is evident that the mixture of iodine and iodic acid, both ordinarily oxidising agents, is able to effect the decomposition of hydrochloric acid with the formation of iodine monochloride.

SOME PECULIARITIES OF SOLUTIONS OF FERRIC SULPHOCYANATE.

By LAUNCELOT ANDREWS, Ph.D.

THE deep blood-red colour of solutions of ferric sulphocyanate has frequently been taken advantage of for the determination of small quantities of iron in river or spring water, in blood, in alloys, in alum-cake, &c.

The earliest method of this kind, so far as I have been able to ascertain, is due to T. L. Herapath, who proposed to determine minute quantities of iron by the addition of potassium sulphocyanate to the acidified solution containing an unknown amount of iron, and also to a standard iron solution of known strength, the latter being then diluted until both showed the same tint.

Very similar methods have been employed or devised by A. Thomsen (*Journ. Chem. Soc.*, xlvii., 493), Ad. Joles (*Arch. f. Hygiene*, xiii., 402), L. Lapique (*Bull. Soc. Chim.*, ii., 295), and by R. R. Tatlock (*Journ. Soc. Chem. Ind.*, vi., 276).

Vierordt ("Quant. Spektralanalyse") suggested a fundamental modification of Herapath's colorimetric method, in that he dispensed wholly with a standard comparison solution, substituting for it a direct spectrophotometric determination of the amount of light of given wave-length, transmitted by a layer of the ferric sulphocyanate solution 1 c.m. thick. In this method the assumption, based upon analogy, is made that the light-absorbing power of the solution is directly proportional to the amount of iron contained therein; or in other words, *that the negative logarithm of the fraction of light transmitted is proportional to the concentration of the solution*, and the assumption seems to be confirmed by Vierordt's observations.

Subsequent investigations by Krüss and Moraht (*Lieb. Ann.*, cclx., 193; "Kalorimetric u. Spektral Analyse," 1891, p. 125), and by Magnanini (*Zeit. Phys. Chem.*, viii., 1) have shown the assumed proportionality to be non-existent in fact. If aqueous solution of ferric sulphocyanate be diluted its colour fades away in a much more rapid ratio than corresponds to the diminishing concentration of the solution. The depth of colour is much enhanced by an excess of either generatrix, *i.e.*, of KSCN or of $FeCl_3$, and, as Magnanini has shown, the change follows the laws of mass action qualitatively and quantitatively.

Magnanini dismisses the affair at this point as a *res adjudicata* assuming that the sulphocyanate is subject, in its solution in water, to a progressive electrolytic dissociation in the ions, Fe and SCN. In accordance with well-known principles, this dissociation must become more complete with increasing dilution, and, of course, the formation of colourless ions from the coloured salt must result in a diminution of the intensity of the colour.

There is, however, another explanation not only possible, but probable. Ostwald has shown that other salts of ferric iron undergo in dilute solution more or less complete hydrolysis into colloidal ferric hydrate and free acid. If this hydrolysis also occurs in solutions, as we have no reason to doubt, of the sulphocyanate, in accordance with the equation—

$$Fe(SCN)_3+3H_2O=Fe(OH)_3+3HSCN,$$

it would offer a complete explanation of the phenomena hitherto observed.

II. *Experimental Part.*

In order to obtain further insight into the nature of the changes occurring upon dilution of solutions of ferric sulphocyanate, and indirectly of solutions in general, it seemed advisable to operate in solutions containing no water.

In such solutions the hydrolysis called for by the second theory given above could not occur, and the electrolytic dissociation called for by the first theory could occur only

in a subordinate degree. Hence both theories would lead us to expect that a solution of stated concentration of $Fe(SCN)_3$ in ether or in amyl alcohol, or in absolute ethyl alcohol, would have a much more intense colour than a solution of the same strength in water, and, second, that the colour would be proportional to the strength.

My observations have confirmed the first prediction, but not the second.

A solution in ether was first prepared containing 4·7 m.grms. $Fe(SCN)_3$ per c.c., both the iron and sulphocyanogen being directly determined and found in accordance. From this solution, which was kept in the dark, the other solutions were prepared and their absorption coefficients determined by repeated observations in a Vierordt spectroscope with double symmetrical slit.

First.—Comparison of absorptive power in amyl alcohol and water solutions. A solution containing 0·0625 m.grms. $Fe(SCN)_3$ per c.c. of amyl alcohol transmitted 42 per cent of light of wave-length 587, or about the same amount as an aqueous solution containing 0·247 m.grms. per c.c., or nearly four times as strong.

I.—*Amyl Alcohol containing* 0·05 *m.grm.* $Fe(SCN)_3$ *per c.c.*, $T = 15°$.

Middle of region.	Per cent transmitted light.	Extinction coefficient.	Absorption ratio K.
617	84·0	0·076	
589	56·2	0·250	0·200
564	42·5	0·372	0·134
517	19·1	0·719	
501	16·0	0·796	

II.—*Amyl Alcohol containing* 0·1 *m.grm.* $Fe(SCN)_3$ *per c.c.* $T = 15°$.

Middle of region.	Per cent transmitted light.	Extinction coefficient.	Absorption ratio K.
617	41·0	0·377	
589	14·8	0·830	0·120
564	6·8	1·167	

III.—*Amyl Alcohol containing* 0·094 *m.grm.* $Fe(SCN)_3$ *per c.c.* $T = 18°$. *Older Solution, stood Forty-eight Hours.*

Middle of region.	Per cent transmitted light.	Extinction coefficient.	Absorption ratio K.
622	61·0	0·215	0·436
599	42·9	0·367	0·263
568	12·2	0·914	0·104
556	9·0	1·045	0·090

IV.—*Ethyl Alcohol* 0·094 *m.grm.* $Fe(SCN)_3$ *per c.c.* $T = 18°$.

Middle of region.	Per cent transmitted light.	Extinction coefficient.	Absorption ratio K.
568	21·6	0·665	
556	12·7	0·896	

Other series of experiments with ethyl alcohol, amyl alcohol, and ether, demonstrated that the absorbent power of solutions of ferric sulphocyanate in these menstrua diminishes more rapidly than the concentration. The amyl alcohol was distilled from phosphoric acid to remove traces of organic bases and then thoroughly dried. Hydrolysis of the ferric salt can therefore not occur.

If electrolytic dissociation occurs, the molecular conductivity of these solutions must increase with diminishing concentration and in proportion to the diminishing light-absorbing power.

The electrical resistance of the same solutions which had been examined optically was therefore determined in a resistance cell of the form described by Arrhenius, by Ostwald's method with Kohlrausch-Wheatstone bridge and telephone. The specific resistance of the amyl alcohol employed was about 100,000,000 ohms per m.m. cube.

All the measurements showed that the molecular conductivity of the non-aqueous solutions examined diminished with increasing dilution and in about the same ratio as the reciprocal of the absorption coefficient, whereas the molecular conductivity should be greater at high dilutions than at low if the tapering off of the colour of the former is due to electrolytic dissociation.

I am not prepared to present final quantitative results at present because my apparatus is not perfectly adapted to the measurements of such high resistances, but there is no reason to question the qualitative results nor the general character of the numerical data. A cell now in course of construction having a much smaller resistance constant than that heretofore in use is expected to furnish results of the desired accuracy.

Ivan Klobukoff (*Zeit. Phys. Chem.*, iv., 429) has observed that solutions of hydrochloric acid in ether and in amyl alcohol exhibit a diminution of molecular conductivity with increasing dilution of the solutions, and has shown that it is not due to any chemical action of the acid upon the alcohol. This phenomenon evidently belongs in the same class with that which I have observed in the case of ferric sulphocyanate solutions.

Neither of the theories as yet advanced seems capable of explaining all the facts, and more extended studies of the spectroscopic and electrical behaviour of other coloured salts in non-aqueous solvents must be made before any theory can be advanced with profit.—*Proc. Iowa Academy of Sciences*, i., Part 4.

ESTIMATION OF CARBONATES AND CAUSTIC ALKALIS IN MIXTURES.

By P. L. ASLANOGLOU.

HAVING had occasion to estimate the above I am led to say, after several experiments, that, taking to total alkalinity with N/10 H_2SO_4 and methyl orange as indicator, then titrating another portion with N/10 H_2SO_4 and phenolphthalein as indicator, and subtracting the latter from the former so as to obtain the amount of carbonate, is a very erroneous method for obtaining any good results.

To prove this I dealt with known quantities; I have made a solution of 5·6 per cent $Na_2CO_3+10H_2O$ and 7·045 per cent NaOH, and titrated 5 c.c. of the solution as above. The following is a specimen of a number of determinations:—

With methyl orange required 107·4 c.c. N/10 H_2SO_4.

∴ 100 c.c. of this solution will require 2148 c.c. N/10 H_2SO_4.

1 c.c. N/10 $H_2SO_4 = 0·004$ NaOH.

$2148 \times 0·004 = 8·592$ per cent total alkalinity.

With phenolphthalein required 95 c.c. N/10 H_2SO_4.

∴ 100 c.c. of this solution will require 1900 c.c. N/10 H_2SO_4.

$1900 \times 0·004 = 7·6$ per cent NaOH present in the solution, and subtracting 7·6 from the total alkalinity, 8·592, the number obtained, 0·992, denotes the amount of NaOH to be calculated for $Na_2CO_3+10H_2O$.

$2NaOH$.	$Na_2CO_3+10H_2O$.
80	286
0·992	x

$$x = \frac{0·992 \times 286}{80} = 3·546 \text{ per cent } Na_2CO_3+10H_2O$$

present in the solution.

Therefore by this experiment there is found—

3·546 per cent $Na_2CO_3+10H_2O$
7·6 „ NaOH,

which is far from the truth.

The following simple method I find acts very well:—

Take the total alkalinity with methyl orange, and which in this experiment is 8·592 per cent.

Then take 25 c.c. of this solution and introduce them into a Schrötter's carbonic acid apparatus along with a drop or two of methyl orange, thus to indicate the end of the action; warm, cool, and weigh; the difference of the weights will be the amount of carbonic acid expelled.

It is found in this case that 25 c.c. give 0·2153 CO_2.

CO_2.	$Na_2CO_3+10H_2O$.
44	286
0·2153	x

$$x=\frac{0\cdot2153\times286}{44}=1\cdot3994\ Na_2CO_3+10H_2O.$$

∴ $1\cdot3994\times4=5\cdot5976$ per cent $Na_2CO_3+10H_2O$ present in the solution.

$Na_2CO_3+10H_2O$.	2NaOH.
286	80
5·5976	x

$$x=\frac{5\cdot5976\times80}{286}=1\cdot5657 \text{ per cent NaOH.}$$

Subtracting this amount from the total alkalinity the NaOH present is obtained.

Total alkalinity $8\cdot592-1\cdot5657=7\cdot0263$ per cent NaOH present in the solution.

Results with Phenolphthalein.

	$Na_2CO_3+10H_2O$.	NaOH.
Original amount	5·6	7·045
Found	3·546	7·6
Difference	2·054	0·555

Results with Schrötter's CO_2 Apparatus.

	$Na_2CO_3+10H_2O$.	NaOH.
Original amount	5·6	7·045
Found	5·5976	7·0263
Difference	0·0024	0·0187

It follows that phenolphthalein over-estimates the caustic alkali by about 0·55 per cent, and therefore under-estimates the carbonate by 2 per cent, which is about the error found.

From the above results one concludes that no carbonates can ever be accurately estimated with phenolphthalein as indicator.

I wish to add here that H_2SO_4 must not be used in dispelling the CO_2 from carbonates, but HCl or HNO_3 which has been freed from nitrous fumes by distilling from urea nitrate is even better.

PREPARATION OF CERTAIN REFRACTORY METALS IN THE ELECTRIC FURNACE: TUNGSTEN, MOLYBDENUM, AND VANADIUM.

By HENRI MOISSAN.

We shall describe in this paper the easy preparation of tungsten, and of molybdenum and vanadium carbides, expecting that the researches which we are conducting on this subject will permit us to make known some new properties of these refractory metals.

Tungsten.

It is known that tungsten may be easily obtained in the state of powder by the reduction of tungstic acid at a red heat in a current of hydrogen. The metallic powder thus obtained has hitherto been melted only with great difficulty. Desprez succeeded in fusing small quantities of tungsten in the arc produced by 600 Bunsen elements and in an atmosphere of nitrogen. Riche has also melted tungsten in the arc produced by 200 Bunsen elements. In the flame of the oxyhydrogen blowpipe tungsten is rapidly oxidised and soon disappears, forming fumes of tungstic acid.

The preparation of tungsten, either as a carbide or pure, is effected with great ease in the electric furnace. The mixture of tungstic acid and charcoal is placed in the crucible of the furnace, and in about ten minutes, with a current of 350 ampères and 70 volts, we obtain a metallic regulus of about 120 grms. If we take the precaution of adding a large excess of oxide, we may obtain in the first experiment the pure metal. But it is preferable to prepare at first a metal slightly carburetted, and to re-melt it in a second operation in presence of a large excess of tungstic acid. Under these conditions we obtain a brilliant metal, very hard, and of a specific gravity of 18·7. If the carbon is in excess, we obtain cast metals of very variable compositions. Four different specimens gave on analysis, carbon to the respective amounts of 0·64, 2·74, 4·56, and 6·33. These cast metals have a brilliant fracture; they are stable in presence of air, and are sometimes covered with a fine blue film of tungsten oxide.

This metal has the curious property of fixing a great quantity of carbon. If we prepare tungsten in presence of an excess of carbon with a current, not of 400 ampères, but of 1000 ampères and 70 volts, we obtain cast metals richer in carbon, specimens of which give on analysis the following values:—17·27, 17·61, 18·27, and 18·81.

Molybdenum.

Pure molybdenum has hitherto been regarded as infusible. Henri Debray had difficulty in melting with the oxy-hydrogen blowpipe a molybdenum carbide containing from 4 to 5 per cent of carbon. In the electric furnace the operation is effected in a few moments.

We set out with pure ammonium molybdate, which on ignition yields an oxide in the state of a grey powder. It is mixed with charred sugar and is heated for seven to eight minutes with a current of 350 ampères and 70 volts. We thus obtain a regulus of cast metal which is easily detached from the crucible. This carbide is very hard; it scratches glass and steel; its fracture is brilliant, and it suffers no change in moist air. Its specific gravity is 8·6.

Its composition is variable, according to the proportion of charcoal in the mixture. Three specimens gave on analysis respectively 9·77, 9·88, and 9·9 carbon.

Vanadium.

The important researches of Roscoe have proved how difficult is the preparation of this element. He has established that on reducing vanadic acid with charcoal we merely obtain a silicide scarcely fusible at the temperature of a good wind furnace. Roscoe has ultimately overcome the many difficulties of this preparation, and has obtained metallic vanadium on reducing vanadium bichloride with pure dry hydrogen. He remarks, however, that metal in powder thus obtained still contains a small quantity of oxygen, and 1·3 per cent of hydrogen.

The preparation of cast vanadium in the electric furnace presented the greatest difficulties. We set out with pure ammonium meta-vanadate, which on ignition yielded an easily fusible vanadic oxide of a yellowish brown colour. This oxide was mixed with the charcoal of sugar. When placed at some centimetres from the arc produced by a current of 350 ampères and 70 volts, the reduction did not take place. It was necessary to cause the arc to play in contact with this powder for twenty minutes; then we only obtained on the surface of the mixture small metallic granules of the size of a lentil.

Much higher tensions were needed. On employing the arc yielded by a machine of 150 horse-power, measuring 1200 ampères and from 80 to 90 volts, we obtained in a few moments a complete reduction of the oxide and a fusion of the carbide.

These cast metals thus obtained gave respectively carbon: 25·47, 25·68, and 17·56.

In these conditions we therefore obtain a vanadium carbide containing as much as 25 per cent of carbon. A very curious fact resulting from the totality of our experiments is that as the temperature rises we tend towards metallic carbide very rich in carbon, the composition of which approximates to the other binary compounds of mineral chemistry.

This vanadium carbide has the specific gravity of 5·3.

In fine, we may from these researches draw an interesting conclusion concerning the fusibility of the refractory metals. Pure chrome is more infusible than platinum, and above chrome we have to place molybdenum, uranium, tungsten, and, lastly, vanadium.—*Bull. Soc. Chim. de Paris*, xi.-xii., p. 857.

ON STAFFORDSHIRE CLAY IRONSTONES.

By R. H. WILSON.

I HAVE recently submitted to chemical analysis samples of three kinds of white ironstone, which are respectively called "top," "middle," and "bottom stone." The samples contain :—

	"Top."	"Middle."	"Bottom."
Ferrous oxide	34·74	41·40	43·70
Ferric oxide	1·48	2·50	3·12
Alumina	5·68	4·50	2·85
Oxide of manganese	1·16	1·08	0·50
Lime	3·28	2·29	2·23
Magnesia	3·20	3·50	3·21
Phosphoric acid	0·48	1·08	0·94
Sulphuric acid	0·22	—	0·07
Carbonic acid	28·24	29·70	32·26
Iron pyrites—			
Sulphur 0·22	—	0·43	—
Iron 0·21			
Silica	18·35	10·27	8·27
Combined water	1·72	1·70	1·77
Moisture	0·50	0·60	0·49
Organic matter and potash (by difference)	0·95	0·95	0·59
	100·00	100·00	100·00

The "top," "middle," and "bottom" stone yield respectively 28·06, 34·16, and 36·17 per cent of iron in the raw ore; or 38·03, 47·18, and 51·20 per cent in the calcined ore. The iron produced (on a small scale) from these ores is of good quality, and would be known in the trade as "best mine pig." The samples submitted to analysis and assay came from the vicinity of Tamworth.

THE DETERMINATION OF VANADIC ACID.*

By E. HINTZ and H. WEBER.

(Continued from p. 157).

IN connection with the foregoing research, Carnot (*Comptes Rendus*) has occupied himself with other compounds of vanadic acid, some of which are of importance in analysis :—

Salts of calcium and magnesium behave similarly to the strontium salts. In dilute solutions they are not precipitated by vanadic acid, but in concentrated and strongly ammoniacal solutions there occurs a partial precipitation. In the separation of vanadic acid from phosphoric or arsenic acid, by separating the two latter as magnesium-ammonium salts a repeated precipitation is requisite.

A separation of vanadic acid from alumina or chromium oxide by precipitation with ammonia or ammonium sulphide is not practicable, nor is it possible by precipitating the alumina as phosphate in a slightly acetic solution.

Uranium salts effect a complete precipitation of vanadic acid, either in an ammoniacal solution or in presence of a small quantity of free acetic acid.

For determining vanadic acid the author renders the solution nearly neutral with ammonia, adds a few grms. of ammonium acetate, as also a sufficiency of uranium nitrate, and heats to ebullition. The yellow precipitate is filtered off, washed with water, dried, and detached from the filter, which is burnt separately. When ignited with access of air, the precipitate has a bright yellow colour and answers to the formula $2VO_3,V_2O_5$, whilst the precipitate dried at 100° has the composition—

$$2VO_3,(N.H_4)_2O,V_2O_5+H_2O.$$

This method effects not merely the separation of vanadic acid from the alkalis and the alkaline earths, but from several metals, such as manganese, zinc, and copper. But in this precipitation with uranium salts, phosphoric and arsenic acids, as also molybdic and tungstic acids, are thrown down along with the vanadic acid.

The separation of vanadic acid from iron is less difficult than that from alumina and chrome. It is effected by precipitating the ferric oxide with ammonia or ammonium acetate or with ammonium sulphide, but the precipitation must be several times repeated.

Manganous oxide forms with vanadic acid an insoluble compound which may serve advantageously for the determination of vanadic acid.

We mix the solution of the vanadic acid in a flask with ammonium chloride and ammonia in slight excess, and heat to ebullition. We then add a solution of manganous sulphate or chloride, also mixed with ammonium chloride, and maintain the liquid in ebullition for two or three minutes. The liquid, which must still have a slight odour of ammonia, is cooled by plunging the flask into cold water and stoppering it. After deposition, the precipitate is filtered off and washed with cold water. The precipitate is of a brownish yellow, and should contain no brown portions, which would show an oxidation of the ammoniacal solution of manganous oxide by the action of the air. After drying, the precipitate becomes light brown, and after ignition a reddish brown. Its composition is $2MnO,V_2O_5$.

The method just mentioned does not admit of a separation of vanadic acid from phosphoric, arsenic, or tungstic acids. It effects, however, an accurate separation from molybdic acid, as the latter remains completely in solution in the ammoniacal liquid, especially if the ebullition has not been kept up too long. For determining the molybdic acid the excess of manganese present is first precipitated with ammonium sulphide, and the molybdenum sulphide is then separated by means of hydrochloric acid.

O. Manasse has published a memoir on the vanadates of the alkaline earths (Inaugural Dissertation, Berlin, 1886, see *Liebig's Annalen*, ccxl., 23), and has used the following methods in the analysis of these salts :—

The barium salts were fused with 3 or 4 parts by weight of sodium carbonate, or potassium-sodium carbonate, the melt was treated with hot water, and the undissolved barium carbonate filtered off. The latter was always impure, and retained on the average 1·5 per cent vanadic acid. The barium carbonate could not be completely freed from vanadic acid even by a repeated fusion. The impure barium carbonate was therefore dissolved in hydrochloric acid, and the baryta separated as sulphate by means of sulphuric acid. The sulphate on examination was found quite free from vanadic acid. A series of experiments was also carried out by opening up the substance with acid potassium sulphate. The substance in question was fused with five or six times its weight of acid potassium sulphate, allowed to stand for a long time over a small flame, and the melt, after cooling, was rinsed out of the crucible with water and a little sulphuric acid.

* *Zeit. Anal. Chemie.*

The barium sulphate thus obtained passed through the filter with extreme ease, but it was in many cases extremely pure, as the vanadic acid present was only from 0·3 to 0·5 per cent. If, after ignition and moistening with acid, the presence of vanadic acid was recognised, the barium sulphate was dissolved in concentrated sulphuric acid, and the solution poured into water. By this treatment the barium precipitate was certainly obtained perfectly free from vanadic acid, but the process is tedious, as the precipitate of barium sulphate did not completely subside until after a day or two days.

The strontium vanadates, which are sparingly soluble in water, were also decomposed by fusion with an alkaline carbonate. As the strontium carbonate thus obtained still retained vanadic acid, it was dissolved in hydrochloric acid, the solution supersaturated with ammonia, and precipitated with ammonium or potassium carbonate. The strontium carbonate thus obtained was free from vanadic acid. The separation of the strontium as sulphate is less satisfactory, as in consequdnce of the necessary addition of alcohol, the filtrate cannot be well used for the volumetric determination of the vanadic acid with permanganate.

Good results were also obtained by boiling the pulverised salts with an excess of a concentrated solution of potassium carbonate. The resulting strontium carbonate was then further treated as above.

For determining the vanadic acid, the filtrates from the strontium carbonate are merely mixed together, supersaturated with sulphuric acid, reduced, and titrated with permanganate.

The double salts easily soluble in hot water, such as the strontium-potassium vanadates, are dissolved in hot water, and the vanadic acid is precipitated with lead acetate. The lead vanadate is dissolved in nitric acid on the filter, the solution evaporated with sulphuric acid until sulphuric vapours escape, diluted, the lead sulphate filtered off, and the vanadic acid determined volumetrically in the filter.

It is advisable to precipitate the lead vanadate in a hot solution and to stir strongly. In a few minutes the sediment clots together, whilst the supernatant liquid becomes clear as water. The lead vanadate is then at once filtered and washed with cold water. If the precipitate is allowed to stand for some time it gradually becomes pale yellow, pulverulent, and passes readily through the filter.

In the filtrate from the lead vanadate, strontium and potassium are determined after the lead has been removed with sulphuretted hydrogen. The potassium sulphate retained traces of vanadic acid.

In determining vanadic acid in calcium salts, the aqueous solution is at once supersaturated with sulphuric acid, and the vanadic acid is determined in the direct manner.

The latter process was also used in the analysis of the magnesium salts. The acid magnesium vanadates do not readily dissolve in cold water, but an addition of a few drops of sulphuric acid effects immediate solution.

(To be continued).

THE ACTION OF LIGHT UPON DYED COLOURS.*

(Continued from p. 155).

CLASS III.—MODERATELY FAST COLOURS. (WOOL).

THE colours of this class show distinct fading at the end of the second period (July 1 to July 31, 1893), which becomes more pronounced at the end of the third period (July 31 to August 26, 1893). A pale tint remains at the end of the fourth "period of exposure" (August 26, 1893, to February 19, 1894), and at the end of a year's exposure the colour has entirely faded, or, at most, mere traces of colour remain.

Azo Colours.

Wool Book III.

Acid Colours.—

2. Orange GT. From toluidine and β-naphthol-monosulphonic acid S. S. and J. 41.
4. *Mandarin GR. extra. From *o*-toluidine-monosulphonic acid and β-naphthol. S. and J. 78.
5. *Orange H. From α-sulphanilic acid and β-naphthol. S. and J. 73.
7. *Orange III. From *m*-nitraniline and β-naphthol-disulphonic acid R. S. and J. 33.
10. Dimethylaniline Orange. From *p*-sulphanilic acid and dimethyl-aniline. S. and J. 74.
11. *Diphenylamine Orange. From *p*-sulphanilic acid and diphenylamine. S. and J. 75.
12. Tropæolin Y. From *p*-sulphanilic acid and phenol. S. and J. 70.
15. *Metanil Yellow. From *m*-sulphanilic acid and diphenylamine. S. and J. 77.
16. Resorcinol Yellow. From *p*-sulphanilic acid and resorcinol. S. and J. 71.
18. *Acid Yellow OO. Constitution not published.
19. *Fast Yellow N. From *p*-toluidine-*o*-sulphonic acid and diphenylamine. S. and J. 79.
28. *Curcumeïn. Nitro-derivative of Diphenylamine Orange. S. and J. 101.
29. *Azoflavin S. Same as Curcumeïn, but more highly nitrated. S. and J, 102.
44. *——. Bromine derivative of Metanil Yellow.
45. Persian Yellow (G). Constitution not published.

Direct Cotton Colours.—

2. Salmon Red. Constitution not published.
3. Congo Orange R. From tolidine, β-naphthylamine-disulphonic acid R and phenol (ethylated). S. and J. 202.
7. Congo Orange G. From benzidine, β-naphthylamine-disulphonic acid R and phenol (ethylated).
10. Toluylene Orange G. From tolidine, *o*-cresotinic acid, and *m*-toluylene-diamine-sulphonic acid. S. and J. 196.
23. Carbazol Yellow. From diamido-carbazol and salicylic acid. S. and J. 181.
24. *Cotton Yellow G. Sodium salt of diamido-diphenyl-urea-disazo-salicylic acid. S. and J. 144.

Wool Book IV.

Mordant Colour.—

24. Mordant Yellow (Cr.). Constitution not published.

Triphenylmethan Colours.

Wool Book III.

Acid Colours.—

33. Aurotin. Sodium salt of tetra-nitro-phenol phthaleïn. S. and J. 314.

Natural Colouring Matters.

Wool Book IV.

Mordant Colours.—

5. Weld (Al.). Reseda luteola (whole plant).

Notes.—The following colours become somewhat duller and apparently darker during the first and second periods of exposure:—Diphenylamine Orange, Metanil Yellow, Fast Yellow N, Azo-flavin S, Acid Yellow OO, and Aurotin. This appearance is only observed when the patterns are examined "underhand," *i.e.*, by looking down into the fabric; when they are examined "overhand," *i.e.*, by glancing along the surface, a normal fading of the colours is observed. This darkening is probably due to the presence of the diphenylamine group in the first four colours

* Report of Committee, consisting of Professor T. E. Thorpe (Chairman), Professor J. J. Hummel (Secretary), Dr. W. H. Perkin, Professor W. J. Russell, Captain W. de W. Abney, Professor W. Stroud, and Professor R. Meldola. (Drawn up by the Secretary). Read before the British Association (Section B), Oxford Meeting, 1894.

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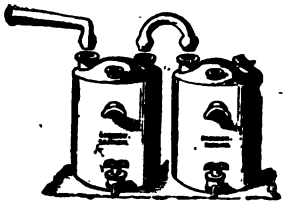

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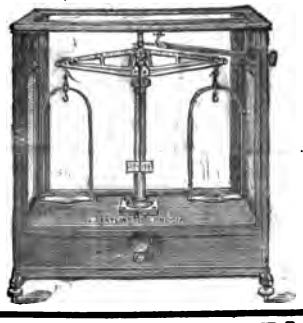

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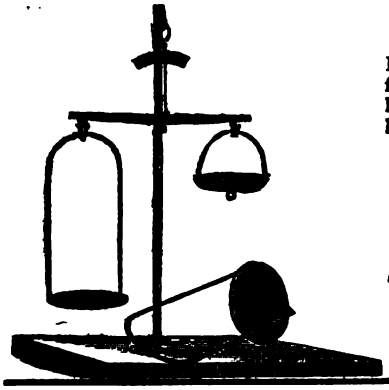

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THE ACTION OF REDUCING AGENTS ON IODIC ACID.*

By CHARLOTTE F. ROBERTS.

I. *The Absorption of Nitric Oxide by Iodic Acid.*

The following investigations were first undertaken with the object of studying the solubility of nitric oxide in iodic acid. Although most chemical authorities agree in the statement that nitric oxide is absorbed by iodic acid with the separation of iodine, there is a certain indefiniteness with regard to the *degree* of solubility, which led me to investigate the subject for myself. Thus, Gmelin-Kraut states that "All the lower oxides of nitrogen decompose iodic acid into iodine and nitric acid, but the decomposition takes place only in presence of a considerable quantity of water," but the *degree of ease* with which the decomposition takes place meets with no comment, and the "considerable quantity of water" seems a somewhat indefinite condition. Kämmerer,† who is the authority referred to for the above facts, and who, some years ago, made a thorough study of iodic acid, says, without referring to any illustrative experiments, "At ordinary temperature, I_2O_5 is reduced only in aqueous solution by nitric oxide, but this gas is without action upon the water-free acid and its solution in concentrated sulphuric acid. At 100° the latter is very slowly, the water-free acid not at all decomposed."

A portion of this latter statement was very easily verified. Some nitric oxide was passed through the dry acid, and other portions were collected and allowed to stand over sulphuric acid solutions of HIO_3 and I_2O_5, without any appreciable separation of iodine.

In order to test the solubility of the gas in *aqueous* solutions of iodic acid, the nitric oxide was prepared in a generator containing potassium nitrate and ferrous sulphate, the air having been previously driven from the apparatus by means of carbon dioxide. The gas was next passed into a Will and Varrentrapp tube containing potassium iodide, and then into a Geissler bulb containing the iodic acid. The experiment was made several times with iodic acid of various degrees of concentration, and always with the same result. There was no evidence of iodine being set free from the iodic acid, though the liquid showed occasionally a barely perceptible tinge of yellow. There was, however, a smaller amount of nitric oxide collected by two or three cubic centimetres than should have resulted from the amount of nitrate used, and on two or three occasions, an odour like that of chlorine was observed about the Geissler bulb, when the apparatus was disconnected, which could only be explained on the supposition that gaseous hydrochloric acid was carried over from the generator through the potassium iodide.

A later experiment in which nitric oxide was collected in a tube containing iodic acid and hydrochloric acid so dilute that no reaction took place between the two acids in the cold, showed that under these circumstances the nitric oxide was absorbed without any separation of iodine and that the liquid became yellow and gave odour like that of chlorine, so that the above seemed a plausible explanation of the disappearance of some nitric oxide in the Geissler bulb without a simultaneous liberation of iodine.

Two or three experiments were then made with the apparatus as before, but with the addition of a new absorption tube containing silver nitrate to prevent the hydrochloric acid from going over into the iodic acid. Still there was no evidence of iodine being set free. It seemed apparent, then, that the nitric oxide was not sufficiently soluble in iodic acid, so that it could be absorbed by simply passing it rapidly through the solution.

To determine whether the gas was soluble upon long contact with the iodic acid or not, different portions were collected in U-tubes closed at one end and filled with solutions of iodic acid of different degrees of concentration. The gas had been collected and allowed to stand over potassium iodide and sodium hydroxide for from twenty-four to forty-eight hours before being transferred to the U-tube, in order to remove completely any other oxide of nitrogen which might be present. Solutions of iodic acid were used in the different U-tubes varying from a saturated solution containing about 50 grms. to 25 cubic centimetres to a rather dilute solution containing not more than 5 grms. to 25 cubic centimetres. There was no apparent absorption as the gas passed up through the liquid, but after the nitric oxide had been standing over the iodic acid for a few moments, iodine appeared on the surface of the liquid. This deposit gradually increased in amount and the liquid rose in the tube, reaching its maximum in 24 hours or less, depending on the amount of gas used.

The result of my experiments, then, has been to show that nitric oxide is absorbed by solutions of iodic acid of any degree of strength, but the reaction takes place slowly even when the gas is confined over the acid, and not at all when passed rapidly through the solution.

II. *The Action of Reducing Agents on Iodic Acid in presence of Hydrochloric Acid.*

It has already been stated that when the nitric oxide was collected over iodic acid mixed with dilute hydrochloric acid, the gas was absorbed, but there was no liberation of iodine, and in some cases an odour like that of chlorine was observed when the tube was opened. A similar phenomenon was noticed with several other reducing agents. It is well known that iodic acid with *strong* hydrochloric acid, or *heated* with dilute hydrochloric acid, forms iodine chloride and may set free chlorine, but in these experiments the dilute acids were used in the cold, and there was no change apparent until the reducing agent was added. Besides the nitric oxide, other substances which had a similar effect were potassium iodide, sodium thiosulphate, arsenious oxide, ferrous sulphate, stannous chloride, and potassium sulphocyanide. If the reducing agent was added in a very concentrated form, iodine was sometimes evolved, and in many cases traces of iodine would first form where the reagent touched the liquid, but would disappear on shaking, and a light yellow liquid would result with an odour like that of chlorine.

The first explanation of this phenomenon that suggested itself was that the iodic acid was not immediately completely deoxidised by the reducing agent, but was first transformed to a lower oxide of iodine (Gmelin-Kraut, *Anorg. Chemie*, i., 2, 290) which was more active and therefore more easily acted upon by hydrochloric acid than the iodic acid itself, and that the chlorine thus set free united wholly or partially with the iodine formed by the first reduction. It was with the object of studying the reduction of iodic acid in the presence of hydrochloric acid that some experiments were undertaken with potassium iodide, iodic acid, and dilute hydrochloric acid. Potassium iodide was chosen as the reducing agent on account of the simplicity of its oxidation products. Approximately N/10 solutions of iodic acid and potassium iodide were used and dilute hydrochloric acid of specific gravity 1·05. The latter acid was so dilute that it could be added in apparently indefinite quantities to the iodic acid without producing any perceptible odour or change of colour.

* Contributions from the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, xlviii., August, 1894.

† *Journ. f. Prakt. Chem.*, lxxxiii., 73.

of gold, nickel, or cobalt, does not interfere. Ferric compounds are more troublesome. In such cases the copper is deposited on a plate of platinum by means of electrolysis; the deposit obtained is moistened with a drop of nitric acid, then with sulphuric acid, heated gently to dryness, and finally treated with hydrobromic acid.

Action of Chlorine in the Cold upon Isobutylic Alcohol.—A. Brochet.—The author studies the properties of dichloric isobutyl oxide, and the behaviour of chloroisobutyral with acetic anhydride and urethane, and the action of hydrochloric acid upon a mixture of isobutylic alcohol and of α-aldehyd chloroisobutyrate.

Synthesis of Mesoxalic Acid and of Bismuth Mesoxalate.—H. Causse.—Already noticed.

Qualitative Detection of the Phenols contained in Officinal Creosote, Beech Creosote, and Oak Creosote.—A. Béhal and E. Choay.—Already noticed.

Formation of Tetrachloroquinon by means of Hexachlorophenol. — Et. Barral. — The author has examined the behaviour of hexachlorophenol with water, sulphuric acid, fuming sulphuric acid, hydrochloric acid, nitric acid, chromic acid, and potassium permanganate. The two last-mentioned reagents do not yield chloranil.

Synthesis of the Hexamethylenic Derivatives, Triethylcyclohexametrione. — A. Combes.— Not suitable for abridgment.

A Correction. — Œchsner de Coninck. — The author wishes to insert in the *Bulletin* for May 20th (463) the words: The nitrobenzoic isomers, like the amidobenzoic isomers, resemble each other two by two.

Researches on the Latex of the Lac-Tree of Tonkin.—G. Bertrand.—This tree belongs to the genus *Rhus*, of the family of Anacardiaceæ. The vapours given off by this latex produce erysipelic ulcerations of the skin. The author has isolated from the original substance a special diastase, which he names Laccase, and from the alcoholid liquid, after separation of the gum and the laccase, a volatile oily substance, Laccol. Laccase appears to be an oxidising diastase. Laccol approximates to the polyatomic phenols.

Detection of Traces of Chlorine.—A. Villiers and M. Fayolle.—Already inserted.

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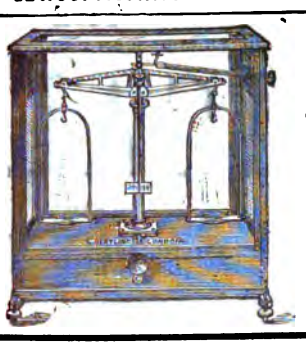

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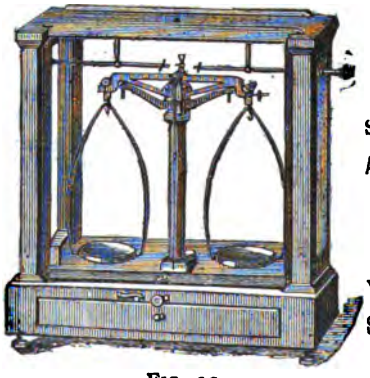

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THE CHEMICAL NEWS.

VOL. LXX., No. 1820.

ESTIMATION BY MOIST GAS.

By WALTER COLQUHOUN, M.A.

IN the CHEMICAL NEWS, vol. lxvii., p. 123, and vol. lxx., p. 101, I pointed out a method of estimating urea by the amount of nitrogen evolved, in which calculations to correct for temperature, pressure, and tension of aqueous vapour were done away with, and amounts of the fluid to be examined taken such that at the temperature and pressure of the estimation each c.c. of N evolved represented one part of urea per 1000. Those interested in estimation by means of moist gas who read my papers will doubtless have observed that the method can be extended to all such estimations, and, since a set of tables for any estimation could be obtained by multiplying the numbers in my urea tables by a constant number, that an empirical formula similar to that which I gave for urea exists in a useful form in most cases. To make my meaning clearer I will give the general investigation, and, for the convenience of those who may wish to construct formulæ to suit their work, I will give a set of tables correct to six places from which others can be derived with little trouble, and consequently the corresponding empirical formula.

Consider the problem: A certain substance, atomic weight = 1, is in solution. How much of the solution must I take at $t°$ C. and p millimetres in order that each c.c. of the substance evolved as gas may represent 1 grm. per litre in the solution or 1 m.grm. per c.c.?

Let K c.c. = amount required.

" W m.grms. = weight of substance to be estimated in the K c.c.

" V_p^t = volume of gas liberated at $t°$ and p m.m.

" V_{760}^0 = vol. of the gas at 0° and 760 m.m.

" F m.m. = tension of aqueous vapour at $t°$.

Then it is obvious—

$$\frac{W}{K} = \text{no. of m.grms. of substance per c.c.}$$

$$= V_p^t \text{ by supposition.}$$

$$\therefore W = K V_p^t \quad \ldots\ldots\ldots \quad \text{I.}$$

and it remains to determine K.

Now—

$$W = V_{760}^0 \times 0{\cdot}0896 \quad \ldots\ldots\ldots \quad \text{II.}$$

and—

$$\frac{V_{760}^0}{V_p^t} = \frac{273\,(P-F)}{(273+t)\,760}$$

$$\therefore V_{760}^0 = \frac{273\,(P-F)\,V_p^t}{(273+t)\,760}$$

and substituting this value in II.—

$$W = \frac{273 \times 0{\cdot}0896 \times (P-F)\,V_p^t}{(273+t)\,760}$$

whence—

$$K = \frac{273 \times 0{\cdot}0896 \times (P-F)}{(273+t)\,760}$$

And if K c.c. of the fluid be used for estimation each c.c. of gas evolved denotes the presence of 1 grm. per litre of the substance estimated. Or if K grms. of any substance containing the substance to be estimated be weighed out, then each c.c. of gas evolved denotes the presence of 0·1 per cent of the substance to be estimated. The accompanying tables give the values of K in the case considered above to six places of decimals, in order that they may stand multiplying in the construction of other tables or for the purpose of very accurate analysis.

Now to get other tables from them, *e.g.*, urea tables. The molecular weight of urea, CON_2H_4, = 60, and the molecule has two atoms of N; also 92 per cent of the N is evolved. We have therefore to multiply each term of the table by—

$$\frac{60}{2} \times \frac{100}{92} = \frac{3000}{92}$$

It will be observed that the difference for pressure is highest at the lowest temperature, and the difference for temperature is highest at the highest temperature. To construct the empirical formula the maximum and minimum difference for pressure should be found and the mean taken, and similarly for temperature. If β and α denote these mean values respectively, and A the amount given by the tables in the neighbourhood of the mean temperature, say, 16° C., then the results of the tables are given as a rule by the formula—

$$N = A + \left(\frac{16-T}{2}\right)\alpha + \left(\frac{P-760}{10}\right)\beta$$

when N = number of c.c. to be measured or grms. to be weighed out.

The urea formula thus becomes, when temperature is measured in degrees C.—

$$N = 2{\cdot}711 + \left(\frac{16-T}{2}\right) \times 0{\cdot}026 + \left(\frac{P-760}{10}\right) \times 0{\cdot}036$$

Pressure in Millimetres.

°C.	720.	730.	740.	750.	760.	770.	780.	790.	800.
2.	0·083647	0·084817	0·085987	0·087158	0·088328	0·089496	0·090669	0·091841	0·093009
4.	0·982950	0·084112	0·085273	0·086435	0·087597	0·088759	0·089921	0·091083	0·092245
6.	0·082251	0·083405	0·084558	0·085712	0·086866	0·088019	0·089173	0·090326	0·091480
8.	0·081551	0·082697	0·083842	0·084987	0·086133	0·087278	0·088424	0·089569	0·090714
10.	0·080838	0·081976	0·083113	0·084250	0·085388	0·086525	0·087662	0·088799	0·089937
12.	0·080136	0·081265	0·082394	0·083523	0·084653	0·085782	0·086911	0·088041	0·089170
14.	0·079409	0·080530	0·081652	0·082773	0·083895	0·085016	0·086138	0·087259	0·088380
16.	0·078670	0·079784	0·080897	0·082011	0·083125	0·084238	0·085352	0·086466	0·087579
18.	0·077941	0·079047	0·080153	0·081259	0·082365	0·083471	0·084577	0·085684	0·086790
20.	0·077267	0·078277	0·079376	0·080474	0·081573	0·082671	0·083770	0.084868	0·085966
22.	0·076415	0·077506	0·078598	0·079688	0·080779	0·081871	0·082962	0·084053	0·085144
24.	0·075619	0·076703	0·077786	0·078870	0·079954	0·081037	0·082121	0·083205	0·084288
26.	0·074812	0·075888	0·076965	0·078041	0·079118	0·080194	0·081270	0·082347	0·083423
28.	0·073983	0·075053	0·076122	0·077191	0·078260	0·079330	0·080399	0·081468	0·082537
30.	0·073134	0·074196	0·075256	0·076320	0·077383	0·078445	0·079507	0·080569	0·081632

Where both temperature and pressure are at their lowest or at their highest the amounts given by the empirical formula in this form diverge about 2-100ths of 1 c.c. from the correct amounts, but so long as the fact is remembered it is unnecessary to complicate the formula by adding other terms to meet exceptional cases.

If it be required to construct tables for the estimation of NH_4 by the amount of N evolved, each term is multiplied by $14 + 4 = 18$, and also, since 97·5 of the gas is evolved (Lunge), by—

$$\frac{100}{97{\cdot}5}$$

The number of c.c. of solution to be measured, or of grms. of a substance containing NH_4 to be weighed, in order that each c.c. of N evolved may represent in the one case 1 grm. of NH_4 per litre, and in the other case of 0·1 per cent of NH_4 in the substance weighed, are given by the formula—

$$N = 1{\cdot}525 + \left(\frac{16 - T}{2}\right) 0{\cdot}015 + \left(\frac{P - 760}{10}\right) 0{\cdot}021$$

and in this formula the divergence is about the hundredth of 1 c.c.

If the number of grms. of N per litre be required, the terms of the table are multiplied by—

$$14 \times \frac{100}{97{\cdot}5}$$

and similarly for other estimations. If n times the quantity given by the formula be used, then of course each n c.c. of gas evolved will represent 1 grm. per litre, or 0·1 per cent as the case may be. This method of analysis may be used with great accuracy by taking multiples of the quantities calculated directly from the tables which I have given. Even with the maximum divergence given by the formula in the case of urea, viz., 2-100ths at 2° and 720 m.m., if we are estimating a 2 per cent solution, we get an error of 0·0148 per cent, and that error can be avoided by remembering the divergence. Of course the error in measurement may equal the divergence of the formula, but that also can be avoided by using multiples of the amounts given.

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By P. L. ASLANOGLOU.

Under ordinary circumstances it is considered sufficient to determine the total acidity of a wine by titration with standard alkali, the fixed acidity after evaporation to dryness on a water-bath and re-solution in water, and the volatile acids by difference, calculating the two former items as tartaric, and the last as acetic, acid. Inasmuch as it is by no means certain that the fixed acidity is really due, even principally, to tartaric acid, and in order to facilitate comparison with other acidities, it is a common custom on the Continent to calculate both the total and fixed acid as SO_3 or as H_2SO_4 (equivalents of decinormal solution, 1 c.c. = SO_3 0·004 grm., H_2SO_4 0·049, $H_2\bar{T}$ 0·0075, $H\bar{A}$ 0·0060, $H_3\bar{C}i$ 0·0064, malic 0·0067, succinic 0·0059).

In England we have seen no advantage in this change, as long as it is distinctly understood that the acidity is mainly due to acid potassium and lime salts of the organic acids, and that the free acids themselves are rarely present, unless they have been added, of which more presently.

A research into the amounts and nature of these acid salts is rarely undertaken, on account of the trouble and time involved. On the other hand, anyone who has executed a large number of analyses of different wines will not have failed to notice the frequent discrepancies between the customary acidity figures and the character and value of the wine as determined by the palate. The better class of wines will sometimes show a higher acidity than coarser kinds that are harsh and sour to the taste. Part of this may be masked by sugar or tannin; part may be due to easily decomposable esters in the older wines, which esters, as is well known, do not taste acid, and yet are broken up by the alkaline solution, and therefore rank in the neutralising power. But I am of opinion that the discordance between the all-important evidence of the palate and the at first sight more exact acidimetical indications, is due to the different effects of the different organic salts on the sense of taste. It is within the knowledge of most people that free tartaric acid has a more raw flavour than citric possesses, and that either of them are less agreeable than a chemically equal acidity caused by cream of tartar. I am undertaking some experiments on this head, on which there is at present little or no exact information. To eliminate as much as possible the personal equation, the articles must be tasted by a number of persons who are ignorant of their composition.

Meanwhile it must be admitted that the acidity figures as ordinarily given have very little meaning. It has long been known that other acids besides acetic and tartaric are constituents of wines, some of which are derived from the juice of the grape itself, others from the agency of different organisms causing the several varieties of fermentation, and even a third class may have been added in the common sophistications. Thus succinic acid is always present as one of the products of the ordinary alcoholic fermentation, butyric may be formed by certain diseases that wine is subject to, malic is largely present in unripe grapes, and citric may enter from the added juices of other fruits. Many books on the concoction of wines give recipes for their manufacture from cider, gooseberries, damsons, &c.; and although the popular idea as to the use of these prescriptions is perhaps as little justified as the superstition about logwood and port, yet there is no doubt that certain extracts called Teinte or Tinto are used in the preparation of some red wines. Hence the value and necessity of estimating, whenever possible, both the nature and the quantity of the different acids present, and of taking into account the bases with which they are combined.

There are three forms in which the acids may exist in wines:—

1. In the free state.
2. As esters or compound ethers, of ethyl and other radicles.
3. As salts of potash or lime.

It is seldom that these latter can be actually separated from the wine; the acid tartrate of potassium and the bimalate of lime are instances in which this can be done. Processes for their separation have been based on concentration of the wine to a syrup and precipitation of the salts by proof spirit; but a difficulty arises in the presence of a considerable amount of sulphate of potash in plastered wines, which, being little soluble in alcohol, is thrown down in the crystalline form along with the organic salts. The process hitherto recommended consists in weighing the total precipitate, then determining the sulphuric acid, calculating it into sulphate of potassium, deducting this weight, and putting down the difference as potassium bitartrate: this is a very incorrect method. Another method is to wash the precipitate with a saturated aqueous solution of cream of tartar, so as to dissolve out the sulphate. Both processes are vitiated by the presence of sulphate of lime. The latter method is also falsified—(1) if the temperature varies; (2) if any evaporation takes place. Yet a third process is to determine the acidity of the precipitate by standard soda, calculating into cream of tartar. The result is

wrong if a malate be present, as the equivalents are different.

I suggest the following simple modification for separating the sulphate first:—Carefully determine the sulphate in 100 c.c. Now take 500 c.c. of the wine, heat to boiling, add the exact amount of a standard solution of $BaCl_2.2H_2O$, to throw down all the H_2SO_4. Keep hot on a sand-bath till the $BaSO_4$ settles, and filter. Chloride of potassium and chloride of calcium are left. Any excess of barium chloride must be carefully guarded against. Divide the filtrate into two parts, evaporate each to a syrup, add with vigorous stirring thrice the volume of proof spirit, and allow to stand for twelve hours. Potassium bitartrate and calcium bimalate will crystallise out in both. Meanwhile prepare cold saturated solutions of each of these two salts, by shaking the fine powders vigorously at intervals with a quantity of water insufficient to dissolve the whole ($KHC_4H_4O_6$ is soluble in 180 parts of water, and $(C_4H_4O_5)_2Ca+8H_2O$ in 50 parts), and a little salicylic acid may be added to keep them. Pour off through small filters the mother-liquors, wash the deposits with proof spirit, transfer to the dishes any small crystals that may be on the filters, dry *in vacuo* over the H_2SO_4, and weigh. The weights should be nearly identical. Now wash one portion with six successive quantities of 10 c.c. each of the $KH\overline{T}$ solution, stirring at intervals with a glass rod, and allowing half an hour's contact each time; the liquid is decanted and allowed to settle, and any deposit which is crystalline is finally washed with a little proof spirit and put back. By this means the potassium bitartrate only will be left, and after weighing may be re-crystallised from hot water. The same process carried out on the other portion with the bimalate solution will leave the calcium bimalate, which may be weighed and then re-crystallised from hot dilute nitric acid. Any indirect process based on calculations by difference of acidities or by burning and determining the ash or the Ca, or K or SO_3, may give figures indeed, but they fail to carry conviction, and many of the recorded ones are quite worthless. There is also a great objection to destroy your product by burning, as it leaves no opportunity for applying tests, nor for control of a mistake. The usual method of testing for free tartaric acid is to measure two separate 100 c.c. of the wine, and to add to one of them two or three drops of neutral potassium acetate solution, then evaporate both, allow to stand, wash the deposits with proof spirit, and weigh them both. Any excess of weight in the second will be due to free tartaric acid, precipitated by the potash. If any gummy matter be precipitated, the acidities of both will have to be taken.

Modified Process for all the Organic Acids.—Very carefully determine the alkalinity of the ash of 50 c.c. of the wine in a platinum dish. Take 7 or 8 litres of the wine, and add an amount of sulphuric acid exactly equivalent to the above alkalinity; this is to ensure all the organic acid being in the free state. Now distil until 9-10ths have passed over. Continue the distillation by steam until the distillate ceases to come over acid.

The Distillate.—Saturate with standard soda, observing the quantity used (carefully prepared litmus-paper is best for an indicator), and then add a slight measured excess of soda, to prevent dissociation and loss of volatile acid in the subsequent evaporation. Evaporate the whole to about 250 c.c., and transfer to a retort. Add 1-40th of the amount of sulphuric acid necessary to saturate the whole, plus the amount required for the excess of potash. Distil according to M. Duclaux (*Ann. Chim. Phys.* [5], ii., 233), all the valeric acid comes over; the largest quantity he found was 6 m.grms. per litre. This can be just neutralised by baryta, evaporated, dried at 130° C., and the barium valerate weighed (by distillation with the calculated amount of H_2SO_4 the valeric acid can be recovered).

M. Duclaux proceeds to recover the remaining volatile acids by successive partial saturations with H_2SO_4 and distillations. The remainder of the process requires a series of tables, which are given in the above paper, and will be also found in Mr. Allen's "Organic Analysis" and in Mr. Blyth's "Food Analysis."

The total volatile acids average about 0·15 to 0·3 per cent, of which over 9-10ths are acetic, and the rest formic, propionic, butyric, valeric, and traces of higher acids. The percentages of Ba in the different salts are:—Formate, 70·25; acetate, 53·73; propionate, 48·41; butyrate, 44·05; valerate, 40·41.

Wines that contain much carbonic acid should be first freed from it by agitation and a current of air (M. Duclaux).

The Residue of Distillation.—This should be about 500 c.c. Transfer hot to a stoppered Winchester quart, previously heated to avoid cracking, together with any sediment that may have fallen; add 1500 c.c. of rectified spirit, boiling hot; put in the stopper, and tie it in; heat for one hour to 80° C. on water-bath, with vigorous shaking at intervals, and filter hot. Repeat with 500 c.c. of alcohol and filter, the first filtrate in the meantime being kept in a stoppered bottle at 80° C., to avoid any possible precipitation. The filtrates contain all the fixed organic acids. Distil off the alcohol, evaporate the remaining liquid by a filter-pump over H_2SO_4 till it is syrupy, transfer to a well-stoppered and strong bottle, and shake with 1 vol. rectified spirit and 2½ vols. rectified ether. Only succinic acid and glycerin dissolve. Distil off the alcohol and ether, neutralise with standard baryta water (if any precipitate, it must be filtered off), evaporate, and extract again with alcohol and ether. Glycerin dissolves, and may be concentrated and weighed. Succinate of barium is insoluble; it may be washed with alcohol and weighed. Identify it (1) by burning a portion and weighing the ash; (2) by decomposing a portion by the amount of sulphuric acid exactly equivalent to the barium, filtering from $BaSO_4$, evaporating, and obtaining the succinic acid. According to M. Pasteur, this acid averages about 1-84th of the alcohol present in a natural wine. There is a risk in the above of loss of succinic acid by volatilisation with steam. The only remedy is to concentrate a smaller quantity, not less than 500 c.c., *in vacuo*, and then extract as above.

The Total Tartaric, Malic, and Citric.—M. Ordonneau finds (*Bull. Soc. Chimique*, 1891, No. 141, p. 241) that white wines of La Vendée contain more malic acid than tartaric, and shows that the former disappears with the ripeness of the grape and age of the wine. M. Manseau (*Rev. Internat. des Falsifications*, Amsterdam, June 15th, 1892) states that malic acid is a general constituent of wines. M. Berthelot (*Bull. Soc. Chimique*, xxiv., 228) reveals a former error in the presence of a salt of tartromalic acid, which is decomposed by dilute H_2SO_4 into calcium tartrate and calcium bimalate. This difficulty is avoided in the above suggested process, because tartromalic acid in the free state is readily broken up, by the boiling it has been subjected to, into its constituents, tartaric and malic.

The residue which has been extracted with alcohol and ether for succinic acid is neutralised with a slight excess of lime-water, in the cold. On standing, calcium tartrate is completely thrown down in a crystalline state, which adheres to the latter, but can be easily rubbed off, collected, and weighed. Boil the filtrate for one hour; any citrate will go down; filter it boiling hot, wash first with boiling water, then with 25 per cent spirit; weigh the calcium citrate. To the filtrate, evaporated to about 200 c.c., add absolute alcohol until there is no further turbidity; allow to stand one hour, and collect and weigh the neutral calcium malate.

Verify each precipitate after weighing, by the ordinary tests. The best proceeding is to recover the free acid from each at once, by warming with the exact equivalent of dilute H_2SO_4 or oxalic acid, then filter and test it. It

is well to insist on this verification, as so many figures have been published which are untrustworthy, because the precipitate weighed was not really of the composition supposed.

THE DETERMINATION OF VANADIC ACID.*

By E. HINTZ and H. WEBER.

(Continued from p. 169).

As already mentioned, Manasse effects the determination of vanadic acid volumetrically by means of solution of permanganate. This method depends on the reduction of an acid solution of vanadates to vanadium tetroxide by sulphurous acid or sulphuretted hydrogen, followed by the oxidation of the tetroxide to vanadic acid by solution of permanganate.

The earliest accounts of this reduction were given by C. Czudnowicz; subsequently H. E. Roscoe and C. Rammelsberg have thoroughly examined the subject.

In order to verify this method the author dissolved a weighed quantity of vanadic acid in potassa-lye, and, after acidulation with sulphuric acid, diluted the liquid to a known volume. Portions of this liquid, each of 150 c.c., and each containing 0·4 grm. vanadic acid, were mixed hot with an excess of aqueous solution of sulphurous acid, as strong as possible, or with concentrated sulphuretted hydrogen water. Reduction took place at once, the liquid taking the blue colour of the tetroxide. In consequence of the great separation of sulphur in the liquid treated with sulphuretted hydrogen, the reaction was in this case less distinctly visible than in case of reduction with sulphurous acid.

The solutions were then boiled until the odour of sulphurous acid had entirely disappeared, or until (in case of sulphuretted hydrogen) lead paper is no longer blackened. After the expulsion of the gases, the solution was diluted to 700 or 800 c.c. with hot water, and immediately titrated with a solution of permanganate, such that 1 c.c. represents about 0·0015 grm. oxygen. On titration, the blue colour of the solution gradually disappeared; it became almost colourless, and took at last a permanent reddish colour. In specimens reduced with sulphuretted hydrogen this red colour disappeared several times, and repeated additions of permanganate were required until the final reaction was reached. On reduction with sulphurous acid this case scarcely ever occurred.

The last traces of sulphurous acid cannot be expelled from the liquid by mere boiling without great difficulty, and on titration they affected the results injuriously. The values found were always a little too high; on the average of five experiments the vanadic acid was found to be 100·18 per cent.

If after the sulphurous acid had been expelled by boiling, a strong current of dry carbonic acid was passed through the liquid for a few minutes, the results were as good as those obtained by the sulphuretted hydrogen method. On the average 99·9 per cent of the vanadic acid were found. The author prefers the method with sulphurous acid, as the colour reaction is much more distinctly visible than in the solution reduced with sulphuretted hydrogen, which always holds sulphur in suspension.

On a prolonged passage of carbonic acid through the solution treated with sulphurous acid, a perceptible oxidation of the vanadium tetroxide was detected, occasioned by the air contained in the carbonic acid.

Arthur Rosenheim, in a research on vanadio-tungstic acid (Inaugural Dissertation, Berlin, 1888), has given details on the determination of vanadic acid and its separation from tungstic acid.

Wolcott Gibbs, in the analysis the vanadio-tungstates, employed for the separation of the two acids the method first used by Berzelius, according to which the vanadic acid (after the decomposition of the vanadio-tungstates by prolonged boiling with ammonia, potassa, and soda-lye) is separated as ammonium vanadate by means of a concentrated solution of ammonium chloride,

On examining this method, Rosenheim arrived at the following results:—

In very concentrated solutions of vanadates, vanadic acid is precipitated by ammonium chloride; small quantities, however, as Roscoe has indicated, remain in solution. When 0·2 grm. of vanadic acid are used, the loss observed was about 0·3 per cent.

In strongly concentrated solutions of tungstates, tungstic acid is not appreciably precipitated by ammonium chloride.

The ammonium vanadate precipitated by ammonium chloride from mixtures of tungstates and vanadates occludes small quantities of ammonium tungstate. Considerable quantities of vanadic acid remain in the solution, and the tungstic acid separated on expelling the ammonium chloride by ignition is converted into a black, stable nitrogen compound of tungsten.

The separation of vanadic and tungstic acids by means of ammonium chloride is therefore not available for accurate quantitative determinations, especially for the analysis of vanadio-tungstates containing large quantities of tungstic acid along with small proportions of vanadic acid.

For the determination of vanadic acid in presence of tungstic acid, Gibbs has used a method depending on the fact that acid, whether free or in combination, evolves chlorine, and is reduced if boiled with concentrated hydrochloric acid. The free chlorine is determined in the usual manner.

F. Mohr was the first who referred to this method, and probably Gibbs assumes, according to Mohr's statements, that vanadic acid is reduced by hydrochloric acid according to the equation—

$$V_2O_5 + 2HCl = V_2O_4 + H_2O + 2Cl.$$

In the first place Rosenheim sought to ascertain whether in fact the reaction takes place according to the equation above cited, by studying the behaviour of concentrated hydrochloric acid with certain pure vanadates and with pure vanadic acid.

From his experimental results it appears that vanadic acid is never reduced by concentrated hydrochloric acid to V_2O_4 or to any of its derivatives, and consequently that a volumetric method depending on the above equation must give false results.

Probably there are formed some of the numerous oxides or chlorides intermediate between V_2O_5 and V_2O_4. The results of the numerous experiments do not, however, entitle us to set up a definite equation, and hence the method is rejected by the author as unfit for quantitative determinations.

Attempts to found a method of determining vanadic acid upon its behaviour with potassium iodide in a slightly acid solution gave no better result.

The above-mentioned volumetric method with permanganate is also applicable to the determination of vanadic acid in presence of tungstic acid.

According to the suggestion of Gibbs, the solution of the salts is first strongly acidified with a mixture of sulphuric and phosphoric acids, then reduced with sulphurous acid or hydrogen sulphide, and finally titrated with permanganate.

In verifying this method the author arrived at the following results:—

If vanadates and tungstates are simultaneously present, the reduction of the vanadic acid takes place more slowly than in pure vanadic solutions. The light blue vanadyl colour is masked by the violet-grey of the partially reduced phospho-tungstic acid. The changes of colour on titration are also modified, and the recognition of the colour of the permanganate is more difficult.

* *Zeit. Anal. Chemie.*

To remove these difficulties, the author dilutes the solution of the vanadic tungstates as much as possible. During titration, the flask is set upon a white support. The final reaction is detected by a distinct reddish shine which is visible by reflected light at the margin of the liquid. On its appearance the burette is read off, and we ascertain, by the further addition of one to two drops, that the reaction is really complete. It is advisible to use a very dilute solution of permanganate—such that 1 c.c. may represent about 0·008 grm. vanadic acid.

On observing these precautions, the results obtained were very accurate, fluctuating between 100·05 and 100·18 per cent. The process, contrary to the statements of Gibbs, has been successfully used by Rosenheim, in the analysis of the vanadio-tungstates.

(To be continued).

OPENING UP PYRITES WITH SODIUM PEROXIDE.

By C. GLASER.

The proposal of M. Hoehnel was examined more closely, as it offered a possibility of avoiding the tedious and repeated evaporation with hydrochloric acid to expel nitric acid from melts with carbonate and nitrate. But it was found that the matter was less simple than it appeared at first sight. A series of experiments was instituted, the results of which, in so far as they are conclusive, were as follows:—

1. Pyrites with 41·12 per cent total sulphur gave, according to Hoehnel's process, only 38·37 per cent. On acidulating the filtrate from the melt, some sulphur was separated out, and a distinct odour of the decomposition products of hyposulphurous acid was recognised. More sodium peroxide was therefore used for the following experiments, at last 5·0 grms. Na_2O_2 to 0·5 grm. pyrites. In order to avoid any loss before acidulation with hydrochloric acid, some c.c. of hydrobromic acid were added, and the liquid was then boiled until nearly all the bromine was expelled. Precipitation with barium chloride then followed in the usual manner. The result was 41·13 per cent. To avoid the destruction of the nickel crucible, it is advisable to heat at first for ten minutes with so small a flame that the mixture in the crucible merely softens and sinters together. It is then heated for fifteen to twenty minutes with a a powerful "roaring" burner. If these precautions are observed, the determinations can be effected without notable injury to the crucible. Towards the end it is necessary to heat the melt so strongly that it enters into waving ebullition. When the attempt is made to avoid this, the brown metallic oxides become black on lixiviation by the re-formation of iron sulphide. The examination of the residue on the filter after separate treatment with hydrobromic acid gave each time a notable quantity of barium sulphate; whilst when the mixture is heated to wavy ebullition, the filtrate passes off colourless, and without the use of hydrobromic acid there appeared on acidulation merely a slight separation of sulphur, whilst the residue insoluble in water proved quite free from sulphur. It is therefore necessary to attend to the following points:—(1) Gentle heat at the commencement of the fusion; (2) towards the end ignition to full ebullition; (3) oxidation by means of hydrobromic acid. A determination can be effected in from two to two and a half hours.

Sodium peroxide may be used conveniently for determining the sulphur in burnt ore. We take to 1 grm. burnt ore 0·5 Na_2O_2 and 2·0 grms. Na_2CO_3, and heat the mass in a nickel crucible with a moderate flame for fifteen minutes. The melt is easily lixiviated, but before acidifying with hydrochloric acid it is recommended to add a few drops of hydrobromic acid. We then precipitate with barium chloride. Watson's method, which Lunge strongly recommends, is not applicable to American ores, but it gives satisfactory results with Spanish pyrites.—*Chemiker Zeitung.*

THE MAGNESIUM VOLTAIC CELL.

By H. N. WARREN.

As regards constancy and, at the same time, economy, perhaps no form of voltaic cell is more marked than that of Daniels, known as the sulphate of copper battery, but the E.M.F. of the cell and its internal resistance greatly impoverish its effects when high voltage is required. Again, the admired contrivances of Bunsen and Grove present serious inconvenience on account of the corrosiveness of the exciting agents employed. Whereas, on the other hand, magnesium possesses far greater reducing action than zinc; in fact, zinc may be readily and completely deposited from its solution by the aid of that element. Hence we might at once suggest the use of that metal in place of zinc for voltaic agency. Again, cupric chloride is much more soluble in water than cupric sulphate, and, at the same time, can be made to offer less resistance.

A combination of the two substances thus enables one to construct a voltaic arrangement giving a voltage equal to a nitric acid battery or bichromate cell, by using a rod of magnesium in place of the customary zinc, inserting the same in the usual manner within a porous pot, the outside receptacle containing a saturated solution of cupric chloride, rendered strongly acid by means of HCl.

The inside division, or porous pot, is charged with a strong solution of ammonium chloride, which dissolves the magnesium uniformly, forming a double chloride, at the same time preventing local action, whilst the copper chloride outside solution is very slowly decomposed. The only drawback is at present the somewhat high price of magnesium.

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A STUDY OF CERTAIN NOVEL PHENOMENA OF FUSION AND VOLATILISATION PRODUCED BY MEANS OF THE HEAT OF THE ELECTRIC ARC.*

By HENRI MOISSAN.

In a series of memoirs inserted in the *Bulletin de la Soc. Chim.*, we have shown that by a sufficient elevation of temperature, obtained by means of the electric furnace, it is possible to effect in a few moments the crystallisation of metallic oxides, the reduction of certain oxides, the fusion of refractory metals, and the distillation of silica and zirconia.

In the present paper we insist especially on the volatilisation of the metals and the metallic oxides.

When it is required to condense the vapours of substances not easily volatilised at high temperatures, we use a metallic tube cooled internally by a current of water. It is known that H. Sainte-Claire Deville, in his researches on crystallisation, obtained interesting results by this method.

In these experiments we made use of a copper U-tube, of 15 m.m. in diameter, traversed by a current of water at a pressure of about ten atmospheres. The curved part of the tube was introduced into the furnace at 2 c.m. from the arc, above the crucible containing the substance to be

* *Bulletin de la Société Chimique de Paris.*

volatilised. A sheet of asbestos pasteboard placed on the aperture which admits the cold tube allowed of the condensation of the metallic vapours issuing from the furnace.

As an instance of the use of the cold tube, we mention the action of heat on the two stable mineral compounds, magnesium pyrophosphate and silicate.

The pyrophosphate was submitted for five minutes to the action of an arc of 300 ampères and 65 volts in the electric furnace. After a few moments, abundant vapours were evolved. The cold tube placed in the apparatus was traversed before the experiment by a current of water at the temperature of 15·4°. At the end of the experiment, when the furnace was still in full action, the temperature of the water was only 17·5°. Under these conditions, the vapours produced in the furnace condensed with the greatest readiness on the cold tube. When it was withdrawn from the furnace we found that it was in great part covered with ordinary phosphorus, which took fire on friction or became slowly oxidised in the air, yielding a syrupy coating, which reduced silver nitrate abundantly. Besides this phosphorus, we were able to detect on the tube the presence of magnesia.

In another experiment we heated asbestos (magnesium silicate containing a little iron) for six minutes in a coke crucible. The current measured 300 ampères and 75 volts. After the experiment there remained in the crucible merely a very small quantity of melted silicate and a ferruginous globule with a brilliant fracture and containing 1·6 magnesium and 7 silicon.

The cold tube was covered with a grey powder containing a large excess of silica, of magnesia, and very small quantities of carbon and silicon. We found spheres of transparent silica, scratching glass and giving distinctly the reaction of silica with a bead of phosphorus salt.

These two preliminary experiments, which we select among many others, prove that the most stable salts are dissociated at the temperature of the arc, and that it is possible to collect the products of their decomposition and to study them with ease.

Volatilisation of Metals.

Copper.—A fragment of copper of 103 grms. is placed in the coke crucible of the electric furnace. It is heated for five minutes with a current of 350 ampères and 70 volts. After a minute or two, flames of 0·04 to 0·05 metre in length issue forcibly at the apertures which give passage to the electrodes on each side of the furnace. These flames are surmounted by torrents of yellow smoke produced by the formation of copper oxide from the combustion of the metallic vapour. After five minutes the current is stopped, when the ingot remaining in the crucible weighs only 77 grms.; 26 grms. have thus been volatilised. All round the crucible, in the horizontal part between the cover and the furnace, we find a broad halo of globules of melted copper, derived from the distillation of the metal. The yellow vapour collected gives up copper oxide to cold dilute hydrochloric acid, and leaves as a residue small spheres of metallic copper, black on the surface, and soluble in nitric acid. On the cold tube we find abundance of metallic copper.

Silver.—It has long been known that silver is volatile at a high temperature. In the electric furnace it may be brought to full ebullition. It then distils more readily than silica or zirconia. We collect abundance of melted globules, an amorphous grey dust, and absorbent fragments.

Platinum. — When heated in the electric furnace platinum melts in a few moments and is quickly volatilised. We collect metallic platinum in small brilliant globules, and in dust on the cooler parts of the electrodes or under the lower brick at a few centimetres from the crucible.

Aluminium.—Heated for six minutes; current of 250 ampères and 70 volts. We obtain on the cold tube a grey powder, slightly agglomerated, which on agitation with water lets subside to the bottom of the vessel minute globules of aluminium. These spheres have a metallic aspect; they are attacked by hydrochloric or by sulphuric acid, with escape of hydrogen. In the vapours escaping from the furnaces we may also collect on the asbestos pasteboard small metallic spheres covered with alumina.

Tin.—Duration of the experiment, eight minutes. Intensity of the current, 380 ampères and 80 volts. When the furnace is in full action, abundant white fumes escape near the electrodes. We find on the tube a small quantity of tin oxide, soluble in dilute hydrochloric acid, small brilliant globules, and a grey fibrous substance forming a felt. This fibrous portion and the metallic spheres consist of metallic tin, and they give off hydrogen on treatment with hydrochloric acid. It is easy to condense on the exterior part of the furnace small globules of metallic tin mixed with oxide.

(To be continued).

DETECTION OF ALKALINE PERCHLORATES ASSOCIATED WITH CHLORIDES, CHLORATES, AND NITRATES.*

By F. A. GOOCH and D. A. KREIDER.

THOUGH perchloric acid in the free state is an exceedingly active body, its combinations with alkaline metals are, as is well known, so characterised by inertness toward ordinary reagents, that in order to effect its detection it has been customary to place dependence either upon the insolubility of the potassium salt in alcohol, or upon tests for the corresponding chloride derived by ignition.

In experimenting at high temperatures upon mixtures of potassium perchlorate with salts of the halogens, we have found it possible to effect the liberation of the halogen to a greater or less degree by the oxygen of the perchlorate, but the amount thus evolved has never been sufficiently complete or regular to warrant the application of the reaction to the quantitative determination of the perchlorate. In two parallel experiments, for example, a mixture of the double chloride of aluminum and sodium with 0·05 grm. of potassium perchlorate evolved in fusion in a tabulated flask (which was fitted by a ground joint to an inlet tube carrying a constant current of carbon dioxide and connected with Will and Varrentrapp absorption bulbs filled with a solution of potassium iodide), an amount of chlorine corresponding to 0·0482 grm. and 0·0460 grm. of the perchlorate. A similar experiment, conducted in an atmosphere of hydrochloric acid gas and carbon dioxide in mixture, yielded chlorine amounting to 0·0477 grm. of the perchlorate. Fusion of the perchlorate with cadmium iodide resulted in the liberation of much oxygen accompanying the iodine, and a mixture of zinc chloride with potassium iodide (melting at about 200° C.), yielded a large evolution of oxygen which was somewhat diminished but not wholly prevented when manganese chloride was included in the mixture. A series of fourteen experiments in which mixtures of the perchlorate with potassium iodide were treated with meta-phosphoric acid (made by heating the syrupy ortho-acid to 360° C.) in an atmosphere of carbon dioxide showed deficits in the amounts of iodine evolved amounting to 1·7 per cent on the average between extremes of 3·6 per cent in excess and 7·7 per cent in deficiency, and these particular experiments doubtless point to a more complete utilisation of the oxygen of the perchlorate than was actually attained owing to the inevitable partial decomposition of hydriodic acid at the temperature necessary to effect the decomposition of the perchlorate.

We have, however, succeeded in developing a simple and delicate method of detecting perchlorates, and one

* Contributions from the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, xlviii., July, 1894.

which may be applied without great sacrifice in delicacy to mixtures of the perchlorates with chlorides, chlorates, and nitrates. It is evident that for a rapid qualitative test, conditions should be so chosen that the effect of atmospheric air shall not interfere with the certainty of the indication. Of the various salts which we have employed, we chose by preference fused zinc chloride, chiefly because while sufficiently energetic in its action upon the perchlorate, it does not, like manganese chloride or the double chloride of aluminum and sodium, evolve chlorine under the influence of ordinary air at the high temperature of the reaction.

In the experiments recorded in Table I., varying portions of a solution of potassium perchlorate were evaporated to dryness in a test-tube and fused with anhydrous zinc chloride. A trap made by cutting off an ordinary two-bulbed straight drying-tube was hung with the larger end downward in the test-tube, after moistening the interior of the bulbs with a solution of potassium iodide. The chlorine evolved during the heating was registered by the iodine set free from the iodide and subsequently washed with a little water from the trap and tested with starch emulsion.

TABLE I.

$KClO_4$ taken. Grm.	Indication by the starch test.
0·00100	Strong
0·00050	,,
0·00020	,,
0·00010	,,
0·00010	,,
0·00005	Distinct
0·00005	,,
0·00003	Trace
0·00003	None
0·00001	,,
0·00000	,,

The test for 0·00005 grm. of potassium perchlorate is sure and distinct; and it is, of course, evident that the presence of a chloride in the original test can in no way interfere with the certainty of the indication. All substances, however, which yield chlorine by decomposition or by the action of the air must be removed or destroyed before the application of the test. We find by experiment that 0·1 grm. of potassium chlorate is completely broken up by treatment with 5 c.m.³ of the strongest hydrochloric acid and evaporation to dryness. Nitric acid does not yield so readily to the decomposing action of hydrochloric acid, and may be detected in the residue after four similar treatments. To destroy nitrates, therefore, we followed the general plan of decomposition employed in a quantitative method for the determination of nitrates previously elaborated in this laboratory (Gooch and Gruener, *Amer. Journ. Sci.*, xliv., 117) and treated the dry substance to be tested with 2 c.m.³ of a saturated solution of manganous chloride in the strongest hydrochloric acid. The liquid was evaporated to dryness, and the residue was again treated similarly with 1 or 2 c.c. of strong hydrochloric acid. This method of decomposing the nitrate is peculiarly advantageous, since the decomposing agent is itself an excellent indicator of the completeness of the work of removal. Two or three treatments serve to remove the nitrate entirely; but before proceeding with the test it is necessary to remove the manganese which has been introduced, inasmuch as manganese chloride will of itself evolve chlorine, by exchange for oxygen, when heated in air. Sodium carbonate in solution answers the purpose of removing the manganese (together with other interfering substances) and the filtrate from the precipitated manganous carbonate leaves on evaporation a residue, which, when treated with the anhydrous zinc chloride, gives indications for the perchlorate if it is present in appreciable amount. The results of a series of tests for potassium perchlorate associated with the chlorate and nitrate of the same element and recorded in the following table.

TABLE II.

$KClO_4$ taken. Grm.	$KClO_3$ taken. Grm.	KNO_3 taken. Grm.	Treatment for the removal of chlorate and nitrate.	Indication of the perchlorate.
0·0005	—	—	By HCl	Strong.
0·0003	—	—	,,	,,
0·0002	—	—	,,	Good.
0·0001	—	—	,,	,,
0·0001	—	—	,,	Trace.
0·0005	0·1	0·1	By HCl + $MnCl_2$	Strong.
0·0003	0·1	0·1	,, ,,	Good.
0·0003	0·1	0·1	,, ,,	Good.
0·0002	0·1	0·1	,, ,,	Trace.
0·0001	0·1	0·1	,, ,,	Trace.
0·0000	0·1	0·1	,, ,,	None.

It is plain that 0·0001 grm. of potassium perchlorate may be found with certainty when associated with 0·1 grm. of the nitrate or chlorate or both.

ON THE

ESTIMATION OF SULPHUR IN PYRITES.*

By THOMAS S. GLADDING.

THERE are two recognised methods for the estimation of sulphur in pyrites which, with various modifications, are chiefly used by commercial chemists at the present time. These are:—

1. The fusion of the ore with a mixture of sodium carbonate and potassium nitrate, solution in water, filtration from iron hydroxide, and precipitation as barium sulphate.

2. The solution of the pyrites ore in aqua regia, or in aqua regia and bromine, and subsequent precipitation as barium sulphate.

The following investigation was undertaken to determine the relative merits of these two methods, and the proper modifications to be observed:—

A chemically pure potassium sulphate was examined for impurities with negative results. 2·7 grms., containing about the amount of sulphur found in 1 grm. of high grade pyrites, were dissolved in 300 c.c. to 400 c.c. water, 5 c.c. concentrated hydrochloric acid added, and a 10 per cent barium chloride solution added, at the rate of one drop per second, to the boiling solution. We obtained after standing over night—

Sulphur .. .. 0·4960 grm.
,, ... 0·4960 ,,

Theory requires sulphur 0·4965. This amount of 0·496 grm. was taken as the quantity of sulphur contained in 2·7 grms. of the potassium sulphate, and the following series of experiments made exactly as above, with the stated additions and modifications. We first investigated the various conditions of the fusion methods.

Series I.—With additions of 5 c.c. nitric acid:—

Sulphur found .. .. .. 0·5007 grm.
,, ,, ... 0·5007 ,,
,, ,, ... 0·5020 ,,

The presence of nitric acid produces results too high, from the dragging down of nitrate salts, probably barium nitrate.

Series II.—With addition of 17 grms. potassium nitrate:—

Sulphur found.. .. .. 0·5066 grm.
,, ,, ... 0·5102 ,,

Series III.—With addition of 15 grms. of fusion mixture, viz., sodium carbonate and potassium nitrate, and

* From the *Journal of the American Chemical Society*, xvi., No. 6.

addition of hydrochloric acid to neutrality and 5 c.c. in excess :—

Sulphur found.. .. .. 0·5005 grm.

Series IV.—With addition of potassium chloride, 6·5 grms.; sodium chloride, 7 grms. :—

Sulphur found.. .. .. 0·4955 grm.
„ „ .. .. .. 0·4950 „
„ „ .. .. .. 0·4966 „

No appreciable error either way.

The above series of experiments show that no *nitric* acid nor nitrates should be present in the solution at the time of precipitation. Series IV. shows that when all nitric acid is expelled then sodium chloride and potassium chloride in solution will not cause error. We have found, however, that the complete expulsion of all nitric acid is a very difficult and tedious operation, requiring repeated evaporations to dryness with excess of hydrochloric acid.

The practical difficulty of removing all the nitric acid, and time and labour required, are serious objections to this method.

The following experiments were made to investigate the conditions of the second or aqua regia method :—

Series V.—With addition of 2 grms. of citric acid :—

Sulphur found.. .. .. 0·4960 grm.
„ „ .. .. .. 0·4960 „

This shows that the citric acid, which is frequently used to keep up any iron present, does not exert a solvent action.

Series VI.—With addition of 2 grms. citric acid, and 0·500 grm. iron, which is about the amount of iron in 1 grm. of pyrites ore.

Sulphur found.. ..	0·4934 grm.	−0·4937 grm.
„ „	0·4937 „	−0·4933 „
„ „	0·4940 „	−0·4937 „
„ „	0·4938 „	—

This shows that the presence of iron causes low results.

The above results were obtained by ignition of the barium sulphate precipitate at low red heat until the filter paper was thoroughly burned. The precipitate was of a buff colour.

On exposing the precipitates to a strong blast for several minutes longer they assumed a decided red colour and lost weight.

The results were found to be :—

Sulphur found.. .. .. 0·4910 grm.
„ „ .. .. .. 0·4913 „
„ „ .. .. .. 0·4900 „

We attribute these erroneous results to the unavoidable dragging down of iron salts (probably iron sulphate) with the barium sulphate, and in place of an equivalent amount of barium sulphate. On ignition, this iron sulphate is decomposed, the sulphuric anhydride is expelled, causing low results, and the remaining iron oxide colouring the residue.

This was corroborated by taking 2·7 grms. potassium sulphate, precipitating as above, drying the precipitate, brushing from the paper, drying at about 300° C., and adding the ash of the filter-paper, which had been burned in a separate dish.

Sulphur found .. .. .. 0·4961 grm.

On heating over the blast lamp for five minutes we found—

Sulphur .. .. 0·4880 grm.

It is evident that the presence of iron in the solution is incompatible with accurate results.

We next tried the method of Lunge and Hurter. They precipitate the iron with ammonia and throw down the barium sulphate in the filtrate.

Series VII.—With addition of 0·5000 grm. iron, precipitation of same with ammonia, and precipitation of barium sulphate in the filtrate :—

Sulphur found .. .. .. 0·4944 grm.
„ „ .. .. .. 0·4935 „

These results were too low. On re-dissolving the ferric hydroxide (on filter-paper) with hydrochloric acid, and adding barium chloride to the filtrate, and standing over night, we obtained a precipitate of barium sulphate, giving—

1. Sulphur .. .. .. 0·0020 grm.
2. „ .. .. .. 0·0021 „

Adding these amounts, we obtained—

Sulphur .. .. 0·4964 grm.
„ .. .. 0·4956 „

The most careful washing failed to wash out all sulphur from the ferric hydroxide, and this solution in hydrochloric acid, and the separate recovery of sulphur contained therein, was found necessary.

These results were the most satisfactory yet obtained. The precipitate of barium sulphate was pure white, pulverulent, and did not lose appreciable weight on prolonged heating over the blast-lamp. In this respect it differs from all precipitates hitherto obtained, demonstrates its far greater purity, and gives us a fixed and *final* result.

A method recently published instructs as follows :—To the solution (about 200 c.c.), heated on a steam-bath and containing 20 c.c. free hydrochloric acid "add barium chloride solution from a burette, drop by drop, stirring briskly. Add thirty-five c.c., and allow the solution to stand one hour on the steam-bath, filter through 10 c.m. paper, and wash three times with hot water. Ignite and weigh barium sulphate." After calculating per cent sulphur, add 0·20 per cent to the result for solubility of barium sulphate in the acidified liquid.

We tested this method, using 2·70 grms. potassium sulphate, 200 c,c. water, 20 c.c. hydrochloric acid, and 0·500 grm. iron. We obtained—

Sulphur .. .. 0·4900 grm.
„ .. .. 0·4898 „
„ .. .. 0·4902 „
„ .. .. 0·4894 „
„ .. .. 0·4905 „

The average loss was found to be about 0·60 per cent, instead of 0·20 per cent as stated. The colour of the precipitate was light buff. On heating over the blast-lamp for five minutes the precipitate assumed a darker colour and lost 0·021 grm. in weight, so that the percentage of sulphur was reduced about 0·30 per cent more. Evidently this method does not produce a pure precipitate of barium sulphate.

The following series of comparative analyses on samples of pyrites received for assay, corroborates the above results. The results given under "Fusion Method" were obtained *without* evaporating to dryness to expel all nitric acid. The results given under "Bromine Method,

Samples.	Fusion method.	Bromine method, No. 1.	Bromine method, No. 2.
1..	52·50	51·45	51·71
1..	52·34	51·30	51·73
1..	52·60	51·45	51·71
1..	—	51·34	51·71
1..	—	51·32	51·68
1..	—	—	51·78
2..	40·92	—	40·50
3..	39·90	39·25	39·60
4..	40·90	39·72	40·00
5..	41·25	40 05	40·40
6..	41·80	40·90	41·10
7..	40·59	39·71	—
8..	42·54	41·94	—
9..	41·41	40·40	—

No. 1," were obtained by solution in nitric acid and bromine, evaporation to dryness with hydrochloric acid, taking up with hot water, plus hydrochloric acid, addition of two grms. citric acid, and precipitation without removing the iron.

In "Bromine Method, No. 2," the iron was removed with ammonia and the barium sulphate precipitated in the filtrate. The ferric hydroxide was dissolved in dilute hydrochloric acid in a separate beaker, heated to boiling, barium chloride added, allowed to stand over night, and the small amount of barium sulphate thus obtained added to the main precipitate.

We see from the above that the "Fusion Method" without expulsion of all nitric acid gives results altogether too high, as was to have been expected.

The "Bromine Method," when iron is not removed, gives results too low by 0·20 per cent to 0·35 per cent. This is in exact agreement with the previous work on pure potassium sulphate. No accurate allowance can be made on this method, as the error will vary with the amount of heat applied in igniting the precipitate of barium sulphate.

In the "Bromine Method, No. 2," the precipitated iron hydroxide was re-dissolved in every case, and an additional amount of sulphur varying from 0·20 per cent to 0·30 per cent was obtained.

The insolubility of barium sulphate in the solution of ferric chloride thus obtained was demonstrated by dissolving 0·027 grm. potassium sulphate in 50 c.c. water, adding 5 c.c. hydrochloric acid and 0·5 grm. iron, precipitating hot, and allowing to stand over night. We found—

1.	Sulphur	0·0049 grm.
2.	„	0·0050 „
3.	„	0·0051 „

The amount actually present was 0·00496 grm.

As a result of the above investigation and of many comparative analyses of pyrites ores extending over several years, we have adopted the following method of assaying pyrites :—

1. Grind the ore to an impalpable powder, dry at 100° C., and keep in well-corked bottles. Ten or fifteen minutes drying is sufficient.

2. Weigh 1 grm., introduce into beaker, cover with watch-glass, and add 10 c.c. bromine solution, mix by rotating beaker, and allow to stand ten minutes in the cold. Add 10 c.c. nitric acid, mix as before, and allow to stand ten minutes longer in the cold. Finally, place the beaker on a water-bath, containing cold water, heat slowly to boiling, and when solution becomes quiet, remove glass after rinsing, and evaporate to dryness. Add 10 c.c. hydrochloric acid, keeping the beaker covered with a glass, and when violent action ceases, again remove the glass after rinsing, and evaporate to dryness once more. Add 1 c.c. concentrated hydrochloric acid and 50 c.c. hot water, digest until solution is complete, filter, and wash with hot water. The filtrate, about 100 c.c., is now saturated with a slight excess of ammonia, allow to stand hot for ten minutes. The precipitated ferric hydroxide is filtered and washed five or six times more on the paper with boiling hot water, the filtrate acidulated with hydrochloric acid in slight excess, heated to boiling, and 50 c.c. barium chloride solution added, one drop per second to the boiling liquid. The solution is allowed to stand over night, filtered, washed, and ignited, the precipitate of ferric hydroxide is also dissolved in dilute hot hydrochloric acid heated to boiling, and 10 c.c. barium chloride solution added. It is allowed to stand over night, and the barium sulphate thus obtained added to the main precipitate. One filter-paper can be used for the two precipitates.

The bromine solution is prepared by dissolving 75 grms. potassium bromide in 50 c.c. water, adding 50 c.c. bromine, stirring, and adding water to 500 c.c. The bromine will nearly all dissolve. Another form of bromine solution used by some is made by saturating aqua regia with bromine. The first solution is the more certain, however, to oxidise all the ore without separation of any sulphur. The barium chloride is in 10 per cent solution.

Thanks are due to our assistants, Mr. H. E. Cutts and Mr. Thomas Brown, for valuable assistance in the analytical work of the above investigation.

THE ACTION OF LIGHT UPON DYED COLOURS.*

(Concluded from p. 170).

Class IV.—Fast Colours. (Wool).

The colours of this class show comparatively little fading during the first, second, and third periods. At the end of the fourth "period of exposure" a pale shade remains, which at the end of the year's exposure still leaves a pale tint.

Nitro Colours.

Wool Book III.

Acid Colours.—

3. *Palatine Orange. Ammonium salt of tetra-nitro-γ-diphenol. S. and J. 8.

Hydrazone Colours.

Acid Colours.—

36. Tartrazin. Sodium salt of diphenyl-*p*-sulphonic-acid-osazone-dioxytartaric acid. S. and J. 19.
39. Nitrazin Yellow. Sodium salt of dinitro-dixylyl-*p*-sulphonic acid-osazone-dioxytartaric acid.

Azo Colours.

Wool Book III.

Acid Colours.—

23. *Acid Yellow. Sodium salt of amido-azo-benzene-disulphonic acid. S. and J. 21.
24. *Fast Yellow. Sodium salt of amido-azo-toluene-disulphonic acid. S. and J. 22.
25. Brilliant Yellow S. Sulphonated Diphenylamine Orange. S. and J. 76.
31. *Milling Yellow OO. Constitution not published.
34. *Milling Yellow. From β-naphthylamine-α-sulphonic acid and salicylic acid.

Direct Cotton Colours.—

11. Titan Yellow R. From thio-*p*-toluidine-sulphonic acid. (Constitution not published).
12. Chrysamin R. From *o*-tolidine and salicylic acid. S. and J. 195.
13. Cresotin Yellow R. From *o*-tolidine and *o*-cresol-carboxylic acid.
16. Chrysophenin. Ethylated Brilliant Yellow from diamido-stilbene-disulphonic acid. S. and J. 156.
17. Cresotin Yellow G. From benzidine and *o*-cresol-carboxylic acid.
19. Diamine Yellow N. From ethoxy-benzidine, phenol, and salicylic acid (ethylated). S. and J. 204.
21. Chrysamin G. From benzidine and salicylic acid. S. and J. 166.
22. *Oriol Yellow. From dehydro-thio-*p*-toluidine-sulphonic acid and salicylic acid. S. and J. 99.
38. Titan Yellow Y. From thio-*p*-toluidine-sulphonic acid. (Constitution not published).

Wool Book IV.

Mordant Colours.—

12. Chrome Orange (Cr.). Constitution not published.
13. Yellow for wool A F (Cr.). Constitution not published.
20. Chrome Yellow (Cr.). Constitution not published.

* Report of Committee, consisting of Professor T. E. Thorpe (Chairman), Professor J. J. Hummel (Secretary), Dr. W. H. Perkin, Professor W. J. Russell, Captain W. de W. Abney, Professor W. Stroud, and Professor R. Meldola. (Drawn up by the Secretary). Read before the British Association (Section B), Oxford Meeting 1894.

Oxyketone Colours.

Mordant Colours.—

25. Galloflavin (Cr.). Oxidation product of gallic acid. S. and J. 242.
26. Alizarin Yellow A (Cr). Tri-oxy-benzophenone. S. and J. 237,

Natural Colouring Matters.

Mordant Colours.—

2. Persian Berries (Cr.).
8. Weld (Sn).

Notes.—In Palatine Orange we meet with the first example of a colour fast to light, the manufacture of which has already been abandoned; possibly some difficulty or expense connected with its manufacture may account for this circumstance.

Yellow for wool AF, applied with aluminium mordant, is very fugitive, while Chrome Orange seems quite as fast as with chromium. Chrome Yellow with aluminium mordant may be classed as a "moderately fast" colour.

Galloflavin with aluminium and tin mordants gives fugitive colours, more especially with aluminium.

CLASS V.—VERY FAST COLOURS.

The colours of this class show a very gradual fading during the different periods, and even after a year's exposure a moderately good colour remains.

Azoxy Colours.

Wool Book III.

Direct Cotton Colours.—

20. Curcumin S. Sodium salt of azoxy-stilbene-disulphonic acid. S. and J. 16.
33. Mikado Orange 3 RO. Constitution not published. S. and J. 18.
35. Mikado Orange GO. Constitution not published. S. and J. 18.

Azo Colours.

Acid Colours.—

13. Orange GG. From aniline and β-naphthol-disulphonic acid G. S. and J. 28.

Wool Book IV.

Mordant Colours.—

10. *Alizarin Yellow R (Cr.). From *p*-nitraniline and salicylic acid. S. and J. 35.
17. *Anthracene Yellow C (Cr.). Constitution not published.
18. *Diamond Yellow R (Cr.). From *o*-amido-benzoïc acid and salicylic acid. S. and J. 231.
19. *Alizarin Yellow GGW (Cr.). From *m*-nitraniline and salicylic acid. S. and J. 34.
21. *Gambine Yellow (Cr.). Constitution not published.
22. *Diamond Yellow G (Cr.). From *m*-amido-benzoïc acid and salicylic acid. S. and J. 230.
23. *Flavazol (Cr.). From *p*-toluidine and salicylic acid.

Direct Cotton Colours.—

14. Brilliant Yellow. From diamido-stilbene-disulphonic acid and phenol. S. and J. 149.
15. Hessian Yellow. From diamido-stilbene-disulphonic acid and salicylic acid. S. and J. 154.
37. Chloramine Yellow. Oxidation product of dehydrothio-toluidine-sulphonic acid.

Oxyketone Colours.

Mordant Colours.—

9. *Alizarin Orange W (Cr.) (Al.). β-nitro-alizarin. S. and J. 251.

Natural Colouring Matters.

Mordant Colours.—

4. *Flavin (Cr.).
6. *Quercitron Bark (Cr.).
7. *Weld (Cr.).
8. *Old Fustic (Cr.).
16. *Xanthaurin (Cr.). Composition not published.

Notes.—The brownish-red given by Alizarin Orange W with chromium mordant becomes, during the first "fading period," distinctly bluer in shade, and hence apparently darker; the altered colour then fades so slowly that even after a year's exposure the faded colour appears almost as dark as the original.

The azo colours in this class which have been dyed on chromium mordanted wool leave, at the end of a year's exposure, faded colours of greater body and fulness than those applied without mordant; this is no doubt due to the inferior fastness of the latter, the faded colours of which are covered with a thin layer of perfectly bleached fibres.

All the artificial azo-mordant-colours in this class were fixed with aluminium as well as chromium mordant, and found to be equally fast to light. They were also applied with a tin mordant, but only in a few cases were satisfactory level colours thus obtained, and these seemed to be inferior to those applied with an aluminium mordant, in point of brilliancy as well as of fastness to light.

SILK PATTERNS.

Most of the foregoing colours were also dyed on silk, and the patterns were exposed to light along with those on wool. The relative fastness of the various colours was, for the most part, the same as on wool, the differences observed being too unimportant to necessitate a special classification for silk. In Class iv., Yellow for wool A F (Cr.) proved to be much more fugitive on silk, whereas Chrysamin R and G, Titan Yellow R and Y, Oriol, Cresotin Yellow R and G, and Chrysophenin appeared to be somewhat faster. In Class iii. the same remark applies to Cotton Yellow G.

The Indian dye-stuff Kamála was an additional one applied to silk, and found to belong to the fugitive class, being very little faster than Annatto.

GENERAL OBSERVATIONS.

The first thing which strikes one when examining these orange and yellow patterns is the comparatively large number of satisfactorily permanent colours.

In the more or less fugitive class are to be found all the basic colours, all the nitro-phenols, with the exception of Palatine Orange, and all the bright yellows derived from the natural colouring matters by means of aluminium and tin mordants, with the exception of those obtained from Weld. Comparatively few azo colours are met with in this group.

The marked alteration in colour from yellow to orange shown in the case of Picric Acid has long been known, and is ascribed to a reducing action of the light. The equally striking change from orange to brown, shown by Aurantia, does not, however, seem to have been previously recorded.

By far the largest number of yellows, ranging from "moderately fast" to "very fast," are to be found among the azo colours. Specially important are those in which salicylic acid is a constituent element, since not only does this impart to the colour the power of forming more or less stable lakes with chromium and aluminium mordants, but it appears frequently to give the colours the quality of fastness to light, even when no mordant is applied. It is a fact of some importance that the colours obtained with aluminium are practically as fast as those fixed with chromium, since the first-named mordant gives much brighter and purer yellows. The tin mordant, so useful in the production of the most brilliant orange and yellow colours obtainable from the natural colouring matters, seems, however, to be of little or no advantage in connection with most of these azo-mordant-colours, no doubt because they are susceptible to the reducing action of the mordant usually employed for wool—viz., stannous chloride.

Very interesting in point of fastness to light are the azoxy colours, and although unfortunately apt to dye wool somewhat irregularly, giving speckled-looking colours, they are admirably adapted for silk and cotton.

Another interesting little group is that which includes Tartrazin, a colour not only noteworthy for its fastness to light, but also because of its brilliancy and purity.

The fastness of Alizarin Orange is worthy of special mention, for it is probably greater even than that exhibited by most other colours of the Alizarin group, and it shows the peculiar darkening action exerted by the light, probably in consequence of the presence of the nitro group.

It is remarkable how few really fast yellows are derived from the natural colouring matters, and these are chiefly the olive-yellows obtained with chromium mordant. The only fast, and at the same time bright, natural yellows are those derived from Weld, and since this dye-stuff is now of little general importance to the dyer its cultivation has become extremely limited, and is gradually being given up; it is fortunate therefore that science has been able to replace it by efficient substitutes, so far, at least, as permanency towards light is concerned.

Our experiments have already abundantly proved that the popular opinion that the coal tar dye-stuffs include only such as yield more or less fugitive colours is entirely false; indeed, it is perfectly safe to assert that coal tar is the source from which the greatest number of colours fast to light are derived at the present time, and this seems to be specially true of the red and yellow colours.

NOTICES OF BOOKS.

British Guiana: Report on the Agricultural Work in the Botanical Gardens, for the Years 1891—92. Georgetown, Demerara: G. K. Jardine. 1894.

This Report gives in detail the work done during the years 1891—92, and summarises the analytical results of the experimental cane cultivation of the previous years. It was found advisable to adopt a lengthened period in order to comprise not only the cultural operations and growth in the field, but also the general results obtained in the laboratory, of the first crop of canes reaped on the experimental manurial plots begun in 1891.

The experiments of the past two years comprised the raising of seedling sugar-canes; the cultivation and analysis of those raised in the immediately preceding years; the cultivation and analysis, again, of all the old varieties; and the starting of the manurial experiments. Of the latter, the results of the first year only are comprised in this Report.

The rainfall of both years was, we note, much above the average, that of last year being the heavier of the two by over twelve inches, when the large total of 128·03 inches was measured. Of equal importance with rainfall is the duration of open sunshine. Sunshine can never be in excess provided it is accompanied by sufficient rain; and it is satisfactory to see that, though the rainfall was excessive, the sunshine was up to the average. The results of the experiments may be briefly shown as follows:—

1. Nitrogen, in the forms of sulphate of ammonia, nitrate of soda, and dried blood, exerted a favourable influence upon the yield of the sugar-cane, and was, doubtless, the manurial constituent the supply of which mainly governed the incremental yields.

2. Where applied in quantities capable of supplying not more than 40 lbs. of nitrogen per acre, sulphate of ammonia and nitrate of soda were of about the same value, both better than dried blood; but where more than 40 lbs. of nitrogen per acre was applied, sulphate of ammonia gave distinctly the better results; about 2½ cwts. per acre appeared to be the best quantity to use. Superphosphate of lime gave considerable increases of yield when added to manurings of nitrogen and potash, the soil appearing to be deficient in available phosphoric acid. Mineral phosphates were tried, but the results were decidedly inferior, and the addition of potash produced but little, if any, effect. The use of lime resulted in largely increased yields, but the profits are expected to be mainly apparent in succeeding crops.

Seventeenth Annual Report of the Connecticut Agricultural Experiment Station, for 1893. Printed by order of the General Assembly. New Haven: Tuttle, Moorhouse, and Taylor. 1894.

The Connecticut Agricultural Experiment Station, which was established in 1877 for the purpose of promoting agriculture by scientific investigation and experiment, continues its useful work.

The Station is prepared to analyse and test fertilisers, cattle food, seeds, milk, &c.; to identify grasses, weeds, moulds, blight, mildews, insects (both useful and injurious); and, in general, to give information on various subjects of agricultural science. The sanitary analysis of water is, however, not undertaken; this is, we think, a mistake; good water is needed in farms (more especially dairy-farms) just as much as in any other locality, and without analysis good and bad waters all appear alike. All work that is for the public benefit is done free of charge, and the results published, work for the private use of individuals being charged for at moderate rates.

During the year ending November 1st, 1893, two hundred and eighty-four analyses of fertilisers and manurial waste products have been made in the laboratory.

On account of the high prices of organic nitrogenous matters, there has been a strong temptation to use inferior materials, such as leather, horn, and wool. Every fertiliser has therefore been specially tested for leather, and also as to its solubility in pepsin solution. A parallel series of tests has been made, to compare the rapidity with which the nitrogenous matters of different fertilisers become soluble in water by putrefactive decomposition, and samples of Indian corn were grown in artificial soils containing these fertilisers, for the purpose of comparing their relative values as regards nitrogen.

In connection with Farmers' Institutes where dairying was discussed, and for private persons, ninety-three samples of milk and thirty-five of cream were examined. A large amount of work has been done in the study of methods of milk-analysis, chiefly for comparing the percentage of milk solids determined by gravimetric methods with that calculated from the percentage of fat and the specific gravity. Experiments have also been carried out on many other subjects, such as the study of the proteids of wheat, rye, beans, cotton-seed, barley, &c.; the prevention of "scab" of apples and pears; the artificial curing of tobacco; the prevention of potato "rot"; the use of sulphur as a preventative against "leaf-blight," of celery, and "mildew" of grapes under glass, &c. A detailed account of all these and many more experiments is given, and, as far as possible, the results have been tabulated so as to render them easy of reference and convenient for comparison.

Science Progress.

The September No. of this periodical contains several interesting articles, among which may be mentioned one on "Snake Poison," by W. Halliburton, F.R.S.; "The Biological Characters of Bacillus Typhosus (Eberth) and Bacterium Coli Commune (Escherich)," by George A. Buckmaster, M.A., M.D.; and "The Measurement of Temperature," by E. H. Griffiths, M.A.

The list of the Titles of Chemical Literature, to which we have previously referred, is herein given for the month of July.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académi des Sciences. Vol. cxix., No. 13, September 24, 1894.

Experimental Researches on the Influence of Low Temperatures on the Phenomena of Phosphorescence.—Raoul Pictet.—At very low temperatures phosphorescence is completely suppressed. The extinction is entire at from $-60°$ to $-70°$. It is certain that the production of phosphorescent light requires a certain movement of the constituent particles of bodies. On refrigeration this movement is annulled, and the phosphorescence disappears.

Revue Universelle des Mines et de la Metallurgie. Vol. xxvi., No. 3.

Analysis of Slags.—O. Textor.—Translated from the *Journal of Analytical and Applied Chemistry*, 1893.

Causes of Disagreement in the Results of Analyses effected by Different Chemists.—Dudley.—The causes are said to be four—imperfect sampling, impurity of the reagents used, injudicious manipulation, and the use of discordant methods. A case is mentioned where a lot of springs guaranteed to contain 0·9 per cent of carbon were found to contain only 0·8 per cent. A second analysis made on turnings taken from the interior of the trial-bar was found to contain 0·9 per cent, so that the external layers of the springs had lost 0·1 per cent. As regards the impurity of the reagents, the author insists on the necessity of making a blank experiment. An instance is given of an analytical error in the determination of silicon, one chemist returning it as 0·14 per cent and another as 0·28. It appears that the first-mentioned analyst, after having evaporated to dryness and re-dissolved in water, allowed the solution to stand for two days before filtration. During this time the silica was re-dissolved, as was shown by experiment; in two days the silica fell from 0·28 to 0·14 per cent, and after six days to 0·06 per cent. The last source of error is due to the use of different methods. Hence the author recommends the elaboration of normal methods, and proposes that when any article is sold on analysis the method of analysis to be employed must be stipulated in the contract in detail.

On Sampling Zinc Dross for Analysis.—L. Rürup (*Chemiker Zeitung*).—The author recommends the ordinary Cornish method of sampling.

On Sampling Metallic Dross for Analysis.—E. Jansch (*Chemiker Zeitung*).—The author recommends the separate analysis of metallic grains found mixed with oxides, &c.

MISCELLANEOUS.

The late Prof. Von Helmholtz.—According to the *Chemiker Zeitung*, the scientific memoirs of this illustrious *savant* will be edited by his former colleague Prof. Arthur Kŏnig, Departmental Superintendent at the Berlin Physiological Institute.

New Books.—Among books for junior students in chemistry is one announced by Messrs. Churchill on "Elementary Qualitative Analysis." It proceeds from University College, Nottingham; the authors being Professor Frank Clowes and Mr. J. Bernard Coleman. The publishers expect to issue it before the end of the year.

The late Dr. C. R. Alder Wright's Collection of Alkaloids.—The valuable Collection of Alkaloids which formed the subject of the well-known and laborious researches of the late Dr. C. R. Alder Wright, F.R.S., have been presented to Dr. A. P. Luff, of St. Mary's Hospital, by Mrs. Alder Wright.

Photography by Artificial Light.—An interesting exhibition is now going on at the offices of "The Photogram," in Farringdon Avenue. The principal exhibits are the various appliances now in use for the purposes of photography by artificial light. One of the chief novelties in the exhibition is Adamson's Incandescent system, in which the arc lamp is replaced by a number of incandescent lamps disposed in a ring. These lamps are run at a much higher temperature than is usual, with the result of producing a pure, steady, white light, which is agreeably toned down by means of a thin white silk screen. Other systems which are shown at work are Slingsby's magnesium flash light, Houghton's reflector arc lamp, the Gwynne-Pilsen arc lamp, and the Incandescent gas lamp. A valuable improvement in underground photography is the Todd-Forret magnesium lamp, by means of which the duration of the flash can be controlled and a longer exposure obtained. A large number of photographs, taken by the various systems, are exhibited, some of which are of great excellence. An ingenious electric re-touching device is also shown. The Exhibition will be open during the whole of October; tickets free on application.

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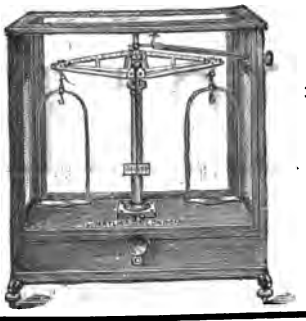

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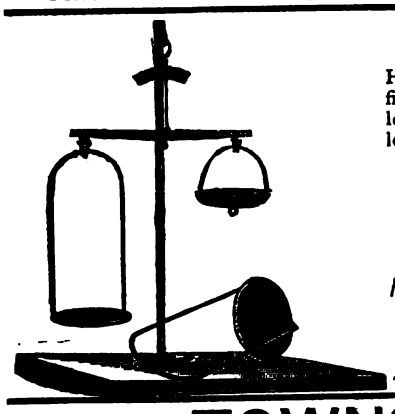

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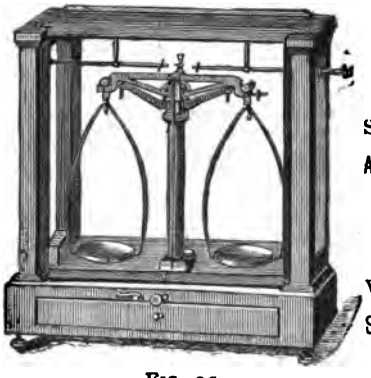

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THE NON-EXISTENCE OF GASEOUS NITROUS ANHYDRIDE.

By W. RAMSAY, Ph.D., F.R.S.

A recent paper by Dr. Lunge and by one of his assistants, Hr. G. Porschnew, treating of the somewhat worn subject—the non-existence of nitrous anhydride in the gaseous state—has been published in the *Zeitschrift für Anorg. Chemie*, 1894, 209. In this paper the authors courteously and amply acknowledge the correctness of the views expressed by Mr. J. Tudor Cundall and myself as long ago as 1885 (*Trans. Chem. Soc.*, xlvii., pp. 187 and 672).

As an example of how Dr. Lunge's views have changed since the date of his rejoinder to these papers, the following quotations are of interest:—

1885.—*Trans. Chem. Soc.*, xlvii., p. 463: "More than 75 per cent of N_2O_3 must be left unchanged when simply vaporising without adding any air, and only a small portion must be dissociated."

1894.—*Zeitschrift für Anorg. Chemie, loc. cit.*, p. 249: "Nitrous anhydride is easily formed at ordinary pressures below −21° C. from nitric peroxide and nitric oxide, and forms an indigo-blue liquid. It is stable at that temperature, but at higher temperatures decomposition begins even under pressure; and this decomposition is complete, or nearly so, when it changes into the gaseous state. The properties of the resulting mixtures are absolutely identical, when brought together with a third substance, with those which would be possessed by gaseous nitric anhydride were it capable of existence."

Compare this last quotation with one from our first paper: "Lastly, nitrogen trioxide does not exist in the state of gas, and probably not as a pure liquid except perhaps at very low temperatures." And, again, in the second paper: "It cannot, of course, be concluded that *no* N_2O_3 is present in the gaseous state, but the near coincidence of the found density with that calculable from Professor Gibbs's formula is a strong presumption that gaseous N_2O_3 is absent, and, indeed, is incapable of existence." And also: "Again, it appears quite as conceivable that NO_2+NO act simultaneously on absorbing agents [the 'third substance,' mentioned above], as that they must first combine before action is possible."

One remark in conclusion. The statement is made in Hr. Porschnew's paper that I have asserted the sparing solubility of nitric oxide in liquid peroxide. In our second paper (p. 678) we state:—"In conclusion, we must remark that, contrary to Dr. Lunge's statement, we do not find that NO is slowly and quite incompletely absorbed by liquid N_2O_4. The rate of absorption is rapid, and the amount greater the lower the temperature." This remark refers to a statement of Dr. Lunge's (p. 464):—". . . An excess of NO, brought in contact with liquid or gaseous N_2O_4, is but slowly and quite incompletely taken up by it to form a substance showing the empirical composition N_2O_3 . . ."

Dr. Lunge and his assistant refer to a later paper of mine on the molecular weight of liquid nitrous anhydride, in which I determined this constant by measuring the depression of freezing-point of the peroxide caused by the presence of a known amount of trioxide, and because I there stated (*Trans.*, lvii., p. 596) that inasmuch as I prepared such a solution by passing nitric oxide into peroxide at a low temperature, I must therefore have volatilised the peroxide. I may remind him that the purpose was not to prepare pure N_2O_3, but a dilute solution of N_2O_3 in N_2O_4. It is unnecessary to state that care was taken not to lose N_2O_4 by evaporation; and that the reason that stronger solutions were not prepared is expressly given:—"(If a larger amount is present) the difficulties of handling become very great, because the tendency to evaporate and decompose is greatly increased." However, this is an unimportant matter.

It is pleasant to terminate a battle, even when it amounts only to a scrimmage between friends; and I have to express my satisfaction that Dr. Lunge and I are now in complete agreement.

University College, Oct. 10, 1894.

ESTIMATION OF CARBONATES AND CAUSTIC ALKALIS IN MIXTURES.

By C. A. SEYLER, B.Sc.

In the Chemical News (vol. lxx., p. 166) appeared an article under the above title, by P. L. Aslanoglou, in which he mentions a method of estimating carbonates and hydrates occurring together, by means of a double titration with phenolphthalein and methyl-orange, and characterises it as "a very erroneous method for obtaining good results." It would be more justly described as a very good method of obtaining erroneous results. He concludes that "phenolphthalein under-estimates the carbonate by about 2 per cent," and that hence "no carbonate can ever be accurately estimated with phenolphthalein as indicator." These conclusions are certainly not warranted by the experiments.

In the first place, having found 3·546 per cent of carbonate instead of 5·6, it is obvious that, if this were correct, the carbonate would be under-estimated to the extent not of 2 per cent, but of 36 per cent. The method appears to be founded on a misconception of a well-known process. Thompson long ago showed that small amounts of carbonate in presence of a large amount of hydrate could be estimated by a double titration with phenolphthalein and methyl-orange, under the proper conditions for preventing loss (or gain) of carbonic acid (Chem. News, xlvii., p. 125). Under these conditions methyl-orange gives the total alkalinity (sum of carbonate and hydrate) and phenolphthalein the sum of the equivalents of the caustic alkali and half the carbonate, since neutrality is reached when all the hydrate is neutralised and the carbonate is converted into bicarbonate. Thus the carbonate present is represented by *twice* the difference of the two titrations.

The author has taken the carbonate as equivalent simply to the difference of the two titrations. Assuming that the right experimental conditions were fulfilled, he therefore found 7·092 and not 3·546, instead of 5·6 actually present, and has therefore *over-estimated* the carbonate to the extent of about 26 per cent. This is just what would happen if all precautions to prevent loss of CO_2 were neglected. These are, to titrate in *very dilute* solution, to run in the acid from a burette with a long spit dipping into the liquid contained in a narrow-mouthed vessel, which is kept in gentle motion without causing air-bubbles, &c.

The author does not describe his method of working, but as he titrates 5 c.c. of a solution nearly half normal with respect to amount of carbonate, it is obvious that the first and most important condition is violated. My own experiments have convinced me that, although phenolphthalein is not an indicator one would choose for the estimation of carbonates, it is quite capable, under the right conditions, of yielding accurate results, especially when it is a question of estimating small

amounts of monocarbonate in the presence of hydrates or bicarbonates. Thus if N/20 or N/10 solutions of sodic carbonate be titrated (best after diluting to 100 c.c. with water free from CO_2 or containing a known small amount) with acid, using methyl-orange and phenolphthalein as indicators, the latter result is, with a close approximation, half the former, as shown by the following experiments:—

(A). 10 c.c. of sodic carbonate solution required 10·35 and 5·1 c.c. N/10 acid with methyl orange and phenolphthalein respectively.

(B). 25 c.c. N/20 sodic carbonate + 75 c.c. distilled water (requiring 0·45 c.c. N/20 Na_2CO_3 to neutralise to phenolphthalein) required 12·1 c.c N/20 acid, and 12·1 + 0·45 = 12·55.

(C). An approximately 5·6 per cent solution of soda crystals was made. Five c.c. were diluted with 95 c.c. water and titrated with phenolphthalein and N/10 acid, keeping the long spit of the burette immersed. Required, 9·55 c.c. N/10 with phenolphthalein = 5·46 per cent soda; with methyl orange, 19·3 c.c. = 5·51 per cent.

By working without the above precautions higher results are obtained, owing to loss of CO_2; thus 5 c.c. soda solution + 95 c.c. water titrated in the ordinary manner required 10 c.c. N/10 acid; 5 c.c. titrated without dilution required 10·7 c.c., equivalent to 6·1 per cent soda.

The method has been recently carefully tested by Dr. Karl Kippenberger (*Zeit. Angew. Chemie*, Aug. 15, 1894), and shown to give good results with solutions of carbonates ranging in concentration from N/250 to N/10, and not only with sodium, but with magnesium carbonate, which is specially important as proving the neutrality of magnesium bicarbonate to phenolphthalein. He has also shown that mixtures of hydrates and carbonates may be accurately titrated in solutions up to N/10 strength, when the relation of hydrate to carbonate is either 9 : 1 or, inversely, 1 : 9 equivalents. I take the following examples from his paper:—

Required—	With Methyl orange.	With Phenolphthalein.	
100 c.c. $MgCO_3$ sol. ..	29·3	14·6 c.c.	N/100 acid.
10 ,, N/10 Na_2CO_3..	10	4·9, 5·0 ,,	N/10 ,,
9 ,, N/10 KOH + 1 c.c. N/10 Na_2CO_3	10	9·5 ,,	N/10 ,,
1 ,, N/10 KOH + 9 c.c. N/10 Na_2CO_3	10	5·4 ,,	N/10 ,,

These experiments fully prove that carbonates can be accurately titrated by phenolphthalein, either alone or in presence of hydrates or bicarbonates.

THE NASCENT STATE.

By JOSHUA C. GREGORY.

In the Chemical News (vol. lxx., p. 152) there appeared a somewhat sweeping denunciation by Dr. L. Andrews of the theory of nascent action. By nascent action, I mean that action of a substance in the nascent state in determining the course of a reaction, which under similar circumstances it would not otherwise exert. The whole conception of the peculiar significance of the nascent state was relegated to the limbo of past superstitions. The sole authority for this sweeping change—for the conception of a nascent state plays no inconsiderable part in chemistry—rested in the fresh interpretation of certain reactions. It has been for some time customary to regard certain reactions as due to the action of nascent hydrogen—such reactions, for example, as the reduction of ferric to ferrous chloride by zinc in acid solution. This view was assailed and declared untenable, and on the strength of this refutation the whole theory of nascent action was generalised as false. Waiving, for the moment, the discussion of these particular instances, we may point out that although in certain cases nascent action may be incapable of, and unnecessary for, explaining certain reactions, it does not follow that this is always the case. *A priori* we should expect to find nascent action. Suppose two substances A and B each having more than one atom to the molecule. Suppose, further, that these two substances unite with but slight evolution of heat. It will not then be difficult to find a certain set of circumstances under which the reaction will not proceed. For example, a certain temperature may be necessary, and a little below this no action will take place. If now, at this lower temperature, circumstances render a less supply of energy necessary for the production of the reaction, it may very possibly be induced to take place. Now, if one of the substances be in the nascent state—that is, without its atoms united into molecules—no energy will be required to break up its molecules, and consequently less energy will be required for the production of the reaction. Thus appears the possibility of nascent action. Does this possibility crystallise into actual fact? In no other way can the superior oxidising power of ozone be explained. We know the ozone molecule to consist of three oxygen atoms, and that when ozone molecules oxidise they part with their third atom of oxygen. We know also that to these atoms belongs the superior power of oxidation; but they differ only from ordinary oxygen atoms in their nascent state. Indeed, the production of ozone itself is not improbably due to nascent action. Its appearance during the action of sulphuric acid on potassium permanganate may be thus accounted for.

The silent electrical discharge not improbably dissociates certain of the oxygen molecules; and their constituent atoms, unable to meet with others anxious for union, prefer to end their wanderings by combining with a molecule. How else can the bleaching action of chlorine be explained? We know that moisture is necessary for this action, we know that the action of the chlorine is to set free oxygen, and we know, further, that this latter oxidises the colouring matter. We know that this liberated oxygen does what ordinary oxygen cannot do, and that it can only differ from the latter in having its atoms free. Further examples might be cited, but let these suffice.

But though Dr. Andrews has not succeeded in disproving nascent action, he appears to have exposed a few fallacies. If copper oxide is actually produced by the action of concentrated sulphuric acid on copper, and if no traces of hydrogen can be detected in the course of the experiment, it is at least probable that what takes place is an oxidation of the copper at the expense of the sulphuric acid, followed by dehydration of the resulting sulphurous acid, thus—

$$Cu + H_2SO_4 = CuO + H_2SO_3$$
$$H_2SO_3 = OH_2 + SO_2$$

Perhaps, too, the necessary strength of acid and height of temperature favour this view. It is interesting, however, in this connection to notice some remarks of Prof. Smithells—formerly made in these pages.

He observed that in the case of a reaction being represented by a double equation, thus—

$$Cu + H_2SO_4 = CuSO_4 + H_2$$
$$H_2 + H_2SO_4 = 2OH_2 + SO_2,$$

he did not conceive the two actions to take place in succession, but, as it were, simultaneously. He compared the two equations to two forces represented by two sides of a parallelogram, and the actual or resultant reaction to the diagonal resultant of the two forces.

Now, if this be a true representation of the case, it may possibly account for Dr. Andrews' failure to detect hydrogen during the production of sulphur dioxide from copper and sulphuric acid. The occurrence of copper oxide, though pointing to Dr. Andrews' explanation, does not preclude the possibility of a concomitant action—such as is at present postulated. Perhaps, too, the different behaviour of mercury and iron towards nitric acid can

hardly be said to demonstrate the non-production of the various reactions by nascent hydrogen. Although the possible production of ammonia by the action of iron on nitric acid, and its impossible production by mercury and nitric acid, may imply specific actions on the parts of the two metals, no conclusive proof of the falsity of the prevalent belief concerning the course of the reaction is thereby afforded. Still, what Dr. Andrews has put forward requires us to revise our views on these points, and possibly we may find nascent action to be less widely extended than we have hitherto believed.

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THE STANDARDISATION OF POTASSIUM PERMANGANATE IN IRON ANALYSIS.*

By CHARLOTTE F. ROBERTS.

For practical work in iron analysis, the standardisation of the potassium permanganate is naturally a very important problem. The best authorities agree in considering that it should be finally standardised on ferric chloride, but the difficulty consists in determining with accuracy the amount of iron in this solution. Though the purest iron which can be obtained commercially is used as the basis, the resulting ferric chloride still contains some silica and phosphorus, which must be eliminated or the amount determined gravimetrically, the process of determining the amount of iron in the ferric chloride solution, upon which the potassium permanganate is finally standardised, thus becomes long and tedious. To obviate this, the following experiments were undertaken in the hope of obtaining the same result by a shorter and more convenient method.

If the potassium permanganate could first be compared with a solution containing a known weight of iron which is finally brought into the same condition as the ferric chloride solution, and then this same potassium permanganate directly titrated with the ferric chloride itself, the necessary accuracy could be obtained without the gravimetric work on the ferric chloride recommended (Blair, "The Chemical Analysis of Iron," pp. 212—216). Since electrolytic iron is undoubtedly the purest form of iron known, it would seem that potassium permanganate titrated against this might be expected to give trustworthy results for the first comparison.

For the production of a definite amount of electrolytic iron two different courses are open to us. Either a weighed amount of a pure iron salt, as ammonio-ferrous sulphate, may be taken and the iron completely precipitated by electrolysis; or an indefinite quantity of the salt may be taken and subjected to electrolysis for a time, and the amount of iron determined by weighing the electrolytic deposit. After some preliminary trials, this second method has recommended itself to me as being much more rapid than the first-mentioned method, and also free from some manipulatory details which render the first difficult to be done with exceeding accuracy.

Some experiments were therefore undertaken to compare the amount of iron determined by direct weighing of the electrolytic deposit with the amount determined by titration of the solution of this same iron with potassium permanganate. The details of the experiments were as follows:—

The solution of potassium permanganate was first accurately standardised with ammonium oxalate which had been shown to give identical results with those obtained by the use of lead oxalate. About 10 grms. of ammonio-ferrous sulphate were dissolved in about 150 c.c. of water, 5 c.c. of a saturated solution of potassium oxalate were added, and then the whole was heated with a considerable quantity of solid ammonium oxalate until a clear solution was obtained. This solution was decomposed in a beaker between two platinum electrodes, the iron being deposited on a piece of platinum foil of a size convenient to be inserted in a rather large weighing bottle, in which it was weighed both before and after the electrolysis. From one and a quarter to one and a half hours, with a current of 2 ampères, was in general found to be sufficient to precipitate from 0·4 to 0·5 grm. of pure iron, and it was found unadvisable to use a current much stronger than 2 ampères, since a higher current showed a tendency to render the deposit less smooth and compact. After washing, drying, and weighing in the usual way, the iron was dissolved in hydrochloric acid, the weighing bottle being used instead of the small flask ordinarily employed in this operation, the oxidised iron was reduced with zinc, and finally titrated with the potassium permanganate solution in presence of sulphuric acid and a large amount of water.

The following table shows the results obtained, the first column giving the weight of the electrolytic deposit of iron, and the second the weight of iron found in the solution of the preceding upon titration with potassium permanganate previously standardised on ammonium oxalate:—

I.	II.	Difference.
0·4357	0·4364	0·0007+
0·3551	0·3559	0·0008+
0·2552	0·2550	0·0002−
0·2898	0·2890	0·0008−
0·1590	0·1599	0·0009+
0·3528	0·3534	0·0006+
0·4498	0·4494	0·0004−
0·5086	0·5085	0·0001−
0·4462	0·4457	0·0005−
0·4226	0·4222	0·0004−
0·5170	0·5165	0·0005−

These results show that the standard of potassium permanganate as determined from pure iron differs very slightly from that obtained with the ammonium oxalate, but the standard obtained in the former way would under ordinary conditions be more satisfactory for work in iron analysis than the latter. A simple and rapid method, then, for standardising the potassium permanganate solution would be to determine its strength, first, by comparison with electrolytic iron in the manner above described, and then by immediate titration with ferric chloride to determine the exact amount of iron in each c.c. of the latter solution. This being ascertained, the ferric chloride solution can be employed at any time for the standardisation of potassium permanganate.

* Contributions from the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, xlviii., October, 1894.

NOTE ON

A FORM OF SILVER OBTAINED IN THE REDUCTION OF THE SULPHIDE BY HYDROGEN.*

By FRANCIS C. PHILLIPS.

It is a well-known fact that many of the metals are reduced from their oxides, sulphides, and other compounds by hydrogen at high temperatures.

In the majority of such cases the form in which the metal is set free depends upon its fusibility. When both the metal and its compound are fusible only at temperatures far above that at which reduction by hydrogen occurs, the reduced metal usually retains the form originally possessed by its compound, becoming, however, somewhat more porous. Iron reduced by hydrogen from

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the oxide, sulphide, or chloride, appears as a porous mass or fine powder. The same is true of platinum and of copper.

In the case of other metals, the character of the original compound may exercise a determining influence on the form of the metal after its reduction.

If silver chloride be heated in hydrogen to about 300° C., reduction occurs with formation of hydrogen chloride. The reduced silver appears as a compact rounded mass, somewhat rough, and having a moderate degree of lustre. On heating precipitated silver sulphide in hydrogen, a decomposition occurs with formation of hydrogen sulphide at about the melting point of silver chloride (450° C.).

The reaction is slow at this temperature, but is more rapid at a somewhat higher heat. The dull black powder soon begins to assume a slightly lustrous appearance, and at the same time changes gradually into a mass of tangled wires or threads, which lose the black colour of the sulphide and exhibit the lustre of highly burnished silver. These vary in thickness from that of the finest hairs to that of coarse sewing-thread. They are so linked and knotted together as to be almost inextricable. Under a microscope it can be readily seen that some of these wires are made up of many smaller ones, which are often imperfectly twisted together, giving the appearance of a rope whose strands have become partly untwisted. Closely-wound coils are often visible. Many of the wires seem to have the smaller ones of which they are composed welded into a single wire, the sides of which then have a fluted or grooved appearance. Owing to the open spaces left in such a mass, a considerable expansion occurs during the reduction. In several trials it was found that the volume of the mass of reduced silver was about three times that of the original sulphide. Experiments made with argentite, the native silver sulphide, using a piece about 3 c.m. thick, led to similar results. The facets of the crystalline mass did not change their shape, nor was their lustre much diminished, but a great number of fine wires of lustrous silver seemed to grow out from the mineral in all directions.

Silver sulphide heated in natural gas gave results like those obtained in hydrogen.

Stephanite, Ag_5SbS_4, although fusible in hydrogen with evolution of a little hydrogen sulphide, yielded no silver at a temperature of dull redness.

Copper sulphide, artificially prepared, was slowly reduced by hydrogen at about the melting-point of barium nitrate (600°), with gradual formation of lustrous threads of copper very similar to those obtained in the case of silver.

The observation that silver and copper may be obtained in the form of wires by reduction of the sulphides is not new.

Opificius (*Chemiker Zeitung*, 1888, 649) announced that such a change occurs.

Bischof (*Annalen der Phys. und Chem.*, 1843, 289) describes experiments in which silver sulphide heated in steam to the temperature of boiling sulphur was reduced, yielding wire silver, the sulphur of the sulphide at the same time being oxidised to sulphuric acid. Bischof compares this change of crystalline argentite into wire-like forms of metal on reduction to the alteration of augite into asbestos.

Hampe (*Chemiker Zeitung*, 1893, 1692) has shown that copper in moss-like forms is produced on heating copper sulphide with filings of the metal to a temperature above the melting-point of copper. The author supposes that copper is dissolved by the fused sulphide and set free again on cooling, being forced out from the fluid interior through the pores of the nearly solid crust in wires or threads. Similar experiments by this author in heating silver with silver sulphide yielded the metal in form of imperfect crystals instead of wires. It is not easy to account for the the fact that silver can assume the form of wires or threads so readily on reduction of the sulphide. The fusing-point of silver is 500° higher than the temperature of reduction, and it does not seem possible that the peculiar form of the silver can have been caused by fusion of the metal. Nevertheless, its appearance suggests that it has passed through a liquid or plastic condition. It might seem possible that by the heat of reaction between the silver sulphide and hydrogen silver, at the moment of its reduction, the silver had been heated locally to fusion. The heat of formation of silver sulphide (three calories) is, however, nearly as great as that of hydrogen sulphide (7·2 calories). Hence the heat of reaction could not suffice to fuse the silver. Nor does it seem probable that the quality of ductility of solid silver could be here brought into play, for there is apparently no force which could be supposed to cause a drawing out of the metal. Hampe's explanation that by being forced out through the pores in a solidified and contracting crust covering a fused interior, copper may have been caused to assume the wire form, cannot apply to silver, for the process here is undoubtedly a gradual one, the sulphide passing without fusion, as reduction occurs into the form of pure silver wires. The results obtained in laboratory experiments suggest an explanation of one mode of occurrence of native metals in veins.

The wire silver found at Zacatecas, in Mexico, may have originated from reactions of such a character.

Hausmann (*Eng. and Min. Journ.*, May 2, 1890) describes the occurrence near Breckinridge, Summit County, Colo., of native gold possessing the remarkable wire-like forms, with fluted or grooved surfaces, so characteristic of silver and copper produced in the laboratory by the reduction of the sulphides by hydrogen.

The change into the fibrous condition at the temperature of the puddling furnace, as cast-iron becomes converted by oxidation into puddled iron, may, perhaps, be considered similar to that which occurs in the reduction of silver sulphide by hydrogen.

The complete removal of impurities from the iron requires a temperature approaching fusion, and the fibres resulting as the metal becomes nearly pure are united into a mass.

THE DETERMINATION OF VANADIC ACID.*

By E. HINTZ and H. WEBER.

(Concluded from p. 179).

In accordance with the results of the foregoing researches, the author proceeded as follows in the analysis of the vanadio-tungstates:—

The determination of the vanadic acid was effected according to the method last mentioned. A very dilute solution of the salt was strongly acidified with phosphoric and sulphuric acids, the vanadic acid was reduced with sulphurous acid, the excess of the latter was expelled by boiling in a current of carbonic acid, and the vanadic acid then determined by titration with permanganate, observing the precautions indicated above.

The determination of the tungstic acid was effected indirectly, the sum of the vanadic and tungstic acids being found, and the latter calculated as difference.

The vanadic and tungstic acids were precipitated with mercurous nitrate from a moderately dilute solution, as neutral as possible, and a few drops of ammonia were then added so as to render the reaction distinctly alkaline. The precipitate was filtered off, and washed with a very dilute solution of mercurous nitrate. The excess of mercury was separated from the filtrate by sulphuretted hydrogen, after acidulation with sulphuric acid, or by the simple addition of hydrochloric acid, and the precipitate was filtered off. Both the mercurial precipitates were dried, and after the very careful incineration of the filters they

* *Zeit. Anal. Chemie.*

were ignited in a porcelain crucible at first slightly and then very strongly, and then weighed.

Before the check weighings, the precipitate was again ignited in an atmosphere of ammonium nitrate in order to oxidise any vanadyl which might have been formed. Both precipitates were ignited together, since it appeared that in the first precipitation the acids were not completely separated, and that generally a part of them was thrown down along with the mercurous sulphide or chloride.

Sometimes a little vanadic acid was still detected in the filtrate from the second mercurial precipitation; it was then determined by titration with permanganate.

The author prooeeded in the same manner in the analysis of the various alkaline salts and barium salts of vanadio-tungstic acid. For the determination of barium, a solution of potassium sulphate was added to the boiling solution of the salts in order to precipitate the barium as sulphate. An addition of sulphuric acid would cause a separation of tungstic acid. Silver vanadio-tungstate was melted with sodium-potassium carbonate for the determination of the vanadic acid, and the acid was then titrated in the usual manner in the aqueous solution of the melt. In order to determine the sum of both acids, the salt was introduced into a boiling solution of sodium nitrate, with which it is transposed into silver nitrate and sodium vanadio-tungstate. The silver was then precipitated by a calculated quantity of solution of sodium chloride, and the sum of both acids was determined in the filtrate in the manner described above.

C. Friedheim considers the determination of vanadic acid in presence of tungstic by titration with permanganate as uncertain, since the final reaction cannot be detected without great difficulty. He recommends the following method for the direct determination of both acids.

To the concentrated solution of the alkaline vanadio-tungstate in a capacious porcelain capsule placed on a boiling water-bath he adds a concentrated solution (as neutral as possible) of mercurous nitrate until the precipitate settles well, and digests it then for about twenty minutes with an excess of mercurous oxide (recently precipitated) in order to neutralise the free acid. When the solution is cold, the precipitate (a mixture of the mercury salts of both acids with an excess of mercurous oxide) is passed through a smooth filter, washed with water to which has been added a few drops of mercurous nitrate, which is quickly effected, then rinsed back from the filter as completely as possible into the vessel used for the precipitation, the contents of which are then evaporated to the consistence of a paste. When cold, it is treated with an excess of the most concentrated hydrochloric acid, stirring carefully, and then covered with a watch-glass and heated for five minutes on a boiling water-bath.

Hereby all the vanadium is converted into vanadyl chloride, nearly all the tungstic acid and the bulk of the mercury pass into solution. The bulk of the mercurous chloride has been converted into mercuric chloride by the action of the chlorine arising from the action of the hydrochloric acid upon the vanadic acid. To the blue solution obtained he then adds much water, by which the dissolved tungstic acid is precipitated almost quantitatively, whilst vanadium and mercury remain in solution. The residue of the precipitate left on the filter is dissolved with hot hydrochloric acid of spec. grav. 1·12, and the solution is poured into the capsule. After standing for twenty-four hours, during which time a little tungstic acid separates out, the precipitate is filtered off, washed with water very slightly acidulated with hydrochloric acid, the residue adhering to the capsule is washed with a little ammonia into a weighed porcelain crucible, the contents are evaporated to dryness on the water-bath, the filter (still moist) is placed in the crucible, dried at 120° in the air-bath, and ignited under the draught-hood with access of air, thus leaving pure yellow tungstic acid.

From the filtrate, after heating to 80°, the mercury is precipitated as sulphide by the prolonged introduction of sulphuretted hydrogen until the deposit subsides completely, the filtered liquid containing vanadyl chloride evaporated to dryness on the water-bath, covered with a watch-glass, and oxidised on the water-bath by treatment with concentrated nitric acid, again evaporated down, the operation repeated at least twice, and the brown hydrated vanadic acid dissolved in water with the addition of a few drops of nitric acid.

The solution is placed in a weighed platinum capsule, evaporated, the residue of the hydrated vanadic acid which remained in the porcelain capsule is dissolved in a minimum of ammonia, added to the main quantity, again evaporated, dried in the air-bath at 120°, and then heated in the oxidising flame with access of air, avoiding fusion at first. The melted mass is finally distributed over the sides by turning the capsule round. When cold, it appears (with the exception of a few darker spots) reddish brown, coarsely crystalline, with the characteristic structure of pure melted vanadic acid. It contains mere traces of tungstic acid ($\frac{1}{10}$ to $\frac{2}{10}$ per cent of the total quantity of tungstic acid). To determine this, the contents of the crucible, after weighing, are treated with dilute sulphuric acid and sulphurous acid at a moderate heat, whereby all the vanadium is dissolved as vanadyl sulphate. The small residue of residual tungstic acid, after filtration, is washed with very dilute sulphuric acid, and weighed. The vanadic solution is evaporated, the sulphuric acid driven off by heat, and the residue ignited as above described, leaving vanadic acid, which melts quite homogeneously.

In the solution filtered off from the mercury salts of the acids, the fixed alkalis present may be determined in a simple manner. The mercury is removed by sulphuretted hydrogen, and the alkali is determined as sulphate. The acid sulphates are converted into normal salts by heating in a current of air charged with ammonia, as recommended by G. Krüss.

If this method is to be applied to meta-tungstates, they must be converted into normal tungstates by boiling and repeated evaporation with ammonia. The solution is then freed from excessive ammonia, and precipitated as explained. Salts of lead and silver are best decomposed with an extremely dilute solution of sodium chloride, and the salts of the remaining metals and alkaline earths by repeated fusion with sodium potassium carbonate; the mixed alkaline extracts are neutralised with acetic acid at a gentle heat, and precipitated as directed.

It may be especially pointed out that the reagents used must be purified with the utmost care. All fixed residues from the mercurial salt, the hydrochloric and nitric acids, and the ammonia would be found along with the vanadic acid, in which case it would melt with great difficulty or not at all.

G. Krüss and K. Ohnmais (*Liebig's Annalen*) employed this process (as devised by Friedheim) in the analysis of the various sulpho-salts of vanadium, and obtained very satisfactory results, both as regards the vanadic acid and the fixed alkalis.

L. L'Hôte (*Comptes Rendus*) uses the volatility of vanadium oxychloride for the detection and determination of vanadium in rocks and ores.

He places an intimate mixture of 4 parts of the substance and 1 part of charcoal in a tube, and heats it to 250° in a suitable furnace, whilst a current of dry chlorine is passed through. Arseniferous minerals must be previously heated to redness, after being, if necessary, made up to a paste with oil. The tube containing the mixture is connected with two Mohr's bulb-tubes containing distilled water. As the vanadium oxychloride forms vanadic acid with water, the presence of vanadium is shown by a reddish colour in the first tube. If only very small quantities of vanadium are present, the liquid in the first bulb-tube remains colourless. For the detection of the vanadium it is then necessary to dissolve the coating formed in dilute hydrochloric acid, to evaporate the solution, and to test the residue with a drop of colourless am-

monium sulphide. This reagent is obtained by introducing turnings or borings of pure silver into small bottles entirely filled with ammonium sulphide. The presence of vanadium is then shown by the characteristic purple colour.

For determining very small quantities of vanadium, L'Hôte reduces the solution acidulated with sulphuric acid with pure zinc, and titrates with a very dilute permanganate. The latter is standardised by means of a dilute solution of vanadic acid of known strength. In the titration especial precautions are needed. The liquids must be warm and the distilled water must be especially pure. To this end it is re-distilled over crystals of permanganate and carefully protected from dust.

If vanadium is present in rather larger quantities, the liquid in the first bulb-tube takes a bluish green colour. The liquid is then mixed with ammonia, and when evaporated to dryness and ignited it yields pure vanadic acid.

ON THE

USE OF MERCURIC OXIDE IN ANALYSIS.*

By E. F. SMITH and PAUL HEYL.

BERZELIUS mentions in his "Lehrbuch" the use of mercuric oxide for the precipitation of zinc, nickel, and cobalt. Volhard recommends that zinc sulphide, as obtained in the ordinary course of analysis, should be dissolved in hydrochloric acid, and that after sufficient concentration mercuric oxide should be added and the mixture evaporated to dryness. On heating, mercuric chloride is expelled, and zinc oxide is left behind. This process has considerable advantages. It abbreviates the ordinary course of the analysis and avoids certain sources of error which may arise on precipitating the zinc with alkaline carbonates. Volhard also mentions (*Liebig's Annalen*, cxcviii., p. 331), that the process might perhaps be advantageously applied to other sulphides. We have endeavoured to solve this question, and we therefore communicate the details of our observations.

The mercuric oxide used in our experiments was prepared according to the instructions of Volhard (*loc. cit.*).

Zinc.

We dissolved not only zinc sulphide, but also weighed quantities of pure zinc oxide, in hydrochloric acid, and after concentrating the liquid to a small volume, we added mercuric oxide in excess sufficient to absorb all the liquid, and distributed it on the moist sides of the crucible. The evaporation was then continued to dryness, and the residue was exposed for ten minutes to the heat of an ordinary iron plate, after which it was strongly heated under a draught-hood. We used a platinum crucible. The results were:—

ZnO used.	ZnO obtained.
0·2180 grm.	0·2179 grm.
0·2155 ,,	0·2156 ,,
0·1437 ,,	0·1441 ,,

Cadmium.

In order to determine cadmium, it is weighed either as sulphide or as oxide. In the former procedure a great expenditure of time is unavoidable, and in the latter there is always danger of loss by volatilisation. The electrolytic method alone yields the best results, but it is rarely used. Volumetric methods are difficult in execution. It seemed therefore advisable to attempt the conversion of the chloride into oxide by means of mercuric oxide. To this end weighed proportions of pure cadmium oxide were dissolved in hydrochloric acid in porcelain crucibles, the solutions were concentrated to a small volume, and an excess of mercuric oxide was distributed on the sides of the crucible. Then followed evaporation to dryness and heating.

CdO present.	CdO obtained.
0·3467 grm.	0·3435 grm.

The difference was evidently due to the volatility of cadmium chloride. In the next determination we took care to coat the sides of the crucible quite closely with mercuric oxide, and dried the mixture on a stove plate before the final heating.

CdO used.	CdO found.
0·1233 grm.	0·1231 grm.

Instead of a porcelain crucible we used one of platinum, and determined the amount of Cd in a hydrochloric solution of known strength.

Cd used.	Cd obtained.
0·1522 grm.	0·1516 grm.
0·1218 ,,	0·1224 ,,

Max Muspratt (*Journ. Soc. Chem. Ind.*, xiii., 211) attempted to apply this method to cadmium. He pronounces it satisfactory for zinc, but useless for cadmium. Cadmium chloride is so volatile that it escapes along with mercuric chloride, and the results are thus too low.

There is no doubt that the use of mercuric oxide with cadmium involves greater difficulties than with any other of the metals which we have examined. Yet if the following precautions are accurately observed not the slightest loss need be apprehended from the volatilisation of cadmium chloride. A platinum crucible must be used, as one of porcelain retains considerable quantities of cadmium chloride adhering firmly to its sides during the evaporation of the solution. But if a platinum crucible is used, scarcely anything creeps up the sides, and the entire quantity of cadmium chloride collects at the bottom of the crucible. The solution of cadmium chloride is evaporated to dryness whether it contains free acid or not, and its sides are spurted with just sufficient water to dissolve the cadmium chloride. A sufficient excess of mercuric oxide is used to absorb the entire solution and to form a thick paste, and the oxide is scattered upon the moist sides of the crucible. It is then dried on a stove-plate, and heated there for about ten minutes until vapours of mercuric chloride begin to escape. It is then heated at first at a very gentle temperature, never allowing the crucible to reach even dull redness, until all the vapours of mercuric chloride are expelled. A full red heat may then be used. as cadmium oxide is not affected.

Manganese.

In analysis, manganese is generally obtained as a sulphur compound, and weighed as mangano-manganic oxide. The conversion of manganese sulphide into oxide can be easily and accurately effected by the use of mercuric oxide, so that the use of alkalis and the protracted washing of the precipitate—which leaves impurities behind—can be dispensed with.

The experiments with manganese were all effected in platinum vessels.

A solution of manganous sulphate, after precipitation with sodium carbonate, yielded per 25 c.c. 0·2109 grm. Mn_3O_4. Other portions of the solution were precipitated with ammonium sulphide, and the manganese sulphide was dissolved in hydrochloric acid. The solution was evaporated to dryness to expel excess of acid, and the residue was taken up in a minimum of water. The sides of the crucible were then, as directed above, coated as completely as possible with an excess of mercuric oxide. It is found that this precaution is absolutely necessary with metals which are so volatile that the portion adhering to the sides of the crucible may escape the action of the mercuric oxide at the bottom of the crucible, which would occasion loss. Cadmium is such a metal.

After thus adding the mercuric oxide it is merely

* *Zeit. für Anorganische Chemie*, vii., 82.

requisite to adhere strictly to the precautions laid down for cadmium. It is advisable to stir the manganese oxide well at a full red heat.

The quantities of mangano-manganic oxide obtained according to this method were, for quantities of 25 c.c. each of the above solution of $MnSO_4$:—

I. 0·2106 grm.	III. 0·2109 grm.
II. 0·2100 ,,	IV. 0·2112 ,,

(To be continued.)

A STUDY OF CERTAIN NOVEL PHENOMENA OF FUSION AND VOLATILISATION PRODUCED BY MEANS OF THE HEAT OF THE ELECTRIC ARC.*

By HENRI MOISSAN.

(Concluded from p. 180).

Gold.—Duration of the experiment, 6 minutes. Intensity of current, 360 ampères and 70 volts. We put 100 grms. gold in the crucible; after the experiment there remained only 95. During the experiment abundant fumes were evolved of a greenish yellow colour. The cold tube was covered with a powder of a dark colour having purple reflections. Under the microscope with a low magnifying power we distinguish clearly small regular globules of melted gold of a fine yellow colour. These globules dissolve readily in aqua regia and give all the indications of salts of gold.

On the asbestos pasteboard where the vapours of the furnace are condensed we found at the hottest point numerous very small globules of metallic gold. Around this part, which had a very distinct yellow colour, was found a red halo, and beyond that a fine deep purple tint.

Manganese.—This metal, to the volatilisation of which M. Jordan has recently called attention, has yielded very interesting results. We describe here only a single experiment, which seemed to us quite characteristic. Duration, 10 minutes; intensity of current, 380 ampères and 80 volts. In the crucible there were placed 400 grms. of manganese. Very plentiful fumes were given off during the experiment, and at the end there remained merely a regulus of metallic carbide weighing only a few grms.

Whenever in the preparation of manganese in the electric furnace we heated too long there was no metal found in the crucible.

Iron.—Duration of the experiment, 7 minutes. Intensity of the current, 350 ampères and 70 volts. We collected on the cold tube a grey powder presenting some brilliant surfaces, very slender and warty, malleable enough to bend under the blade of a knife, mixed with a grey powder having the colour of iron reduced by hydrogen. This powder became brilliant under the burnisher, and the entire specimen dissolved in dilute hydrochloric acid, with a discharge of hydrogen.

On the asbestos pasteboard on which the metallic fumes were condensed we collected small globules of magnetic oxide and spheres of the same compound of a black colour and a wrinkled surface.

Uranium.—Duration of the experiment, 9 minutes. Intensity of the current, 350 ampères and 70 volts. We collect upon the cold tube small metallic globules, full and abundant, mixed with a deposit of grey powder easily soluble in acids, with an escape of hydrogen. The solution presents all the characters of uranium salts. On the asbestos pasteboard we find numerous yellow globes which, if crushed in an agate mortar, lose a crust of oxide, become grey, and take a metallic aspect. These globules of distilled uranium do not contain carbon and are not attracted by the magnet.

* *Bulletin de la Société Chimique de Paris.*

Non-Metals.

Silicon.—With a current of 380 ampères and 70 volts we can effect the volatilisation of silicon. We find upon the cold tube small globules of melted silicon, soluble in the mixture of nitric and hydrofluoric acids. These globules are mixed with a grey dust and a small quantity of silica. If we collect the vapour upon asbestos pasteboard we see that the chief part of the silicon has been converted into silica.

Carbon.—Duration of experiment, 12 minutes. Intensity of current, 370 ampères and 80 volts. On heating a crucible filled with coarse fragments of charcoal all the mass of carbon is quickly converted into graphite. After the experiment we find upon the cold tube slender plates, very light, translucid, and presenting a maroon colour by transmitted light. M. Berthelot, in his numerous experiments on the progressive condensation of carbon, has already indicated the existence of a light carbon of a maroon colour. This substance is separated by dilute hydrochloric acid from the lime which is volatilised at the same time. The residue thus obtained, the study of which we are pursuing, burns readily in oxygen, producing carbonic acid.

Oxides.

The researches above indicated on the crystallisation of oxides abundantly demonstrate the volatility of these oxides. We will put it in evidence for the oxides previously regarded as infusible, lime and magnesia.

Lime.—With a current of 350 ampères and 70 volts we obtain the volatilisation of lime in from 8 to 10 minutes. Under these conditions we collect lime on the cold tube in the form of an amorphous dust, presenting no globules. Vapours of calcium oxide escape from the furnace in plenty. With a current of 400 ampères and 80 volts the experiment is effected in 5 minutes.

Finally, with a current of 1000 ampères and 80 volts we may volatilise in 5 minutes 100 grms. of calcium oxide.

Magnesia.—Magnesia is less readily volatile than lime. Its boiling-point is very near its point of fusion. As soon as the magnesia is melted it emits vapours which condense on the cold tube. This experiment is effected with a current of 360 ampères and 80 volts. This distillation is very rapid if we employ currents of 1000 ampères and 80 volts.

Conclusions.

In fine, at the high temperature produced in our experiments by the electric arc the elements hitherto regarded as the most refractory are volatilised. The most stable compounds of mineral chemistry disappear in the electric furnace either by dissociation or by volatilisation. Nothing remains to resist these high temperatures except a series of new compounds, perfectly crystalline, of an exceptional stability, the properties of which we shall soon describe. These bodies are the metallic borides, silicides, and especially carbides.

Daubrée has already shown that the carbon of all our present organic compounds was originally existent in the state of metallic carbides. The electric furnace seems to reproduce the conditions of that remote geological epoch. It is probable that such compounds exist on stars of high temperatures. We will add that at the same period the nitrogen would be met with in the form of metallic nitrides, whilst probably the hydrogen existed in great quantity in a free state in a complex gaseous medium containing hydrogen carbides.

An Indian Chemical Department.—According to an Indian contemporary the question of the formation of a chemical department for the whole of India is under final consideration, and will be submitted to the Secretary of State during the current season. The question has arisen owing to difficulty having been experienced in supplying chemical examiners for the various Governments at short notice to fill "leave" vacancies.

ON THE

PRODUCTION AND MEASUREMENT OF GOLD AND OTHER METALLIC SPHERES TO DETERMINE THEIR WEIGHT.*

By G. A. GOYDER, Adelaide, South Australia.

DURING 1885 a number of samples of ore and tailings were sent to me for assay. Many of them were small samples and only contained a very little gold; and as under these circumstances an accurate assay could not be made in the ordinary way on those small samples running only a few pennyweights to the ton, the method described below was devised by me, and proved so successful that it was communicated in a paper to the Royal Society of South Australia in 1886, and a copy sent to the Editor of the CHEMICAL NEWS, in which journal it was printed in the same year, but owing to the indistinctness of my signature it was there attributed to Mr. G. A. Gozdorf, and from thence it has since been reprinted in other journals and books under the same name.

In order to make ready use of this process a table was found to be necessary. The paper has therefore been recast, with the addition of such tables as appeared to me likely to be useful. The tables were carefully calculated out under my supervision by my assistant, Mr. J. W. Moule.

In practice this method of measuring gold has proved very much more accurate than the ordinary method of weighing for samples yielding under 5 dwts. per ton and quite as accurate up to 1 oz., and has lately proved very serviceable in assaying tailings and solutions from the cyanide process for extracting gold.

In making assays for gold, where the amount of gold is very small a little silver is required in which the gold may be collected. As nearly all commercial litharge contains silver, it is rarely necessary to add any separately for this purpose. The litharge I at present use contains at the rate of 6 dwts. of silver and ¼th gr. of gold per ton.

Having obtained a prill in which the amount of gold is a third, or less than the silver, the prill is boiled in dilute nitric acid in a porcelain capsule to dissolve the silver, and where the amount of gold is more than 1 dwt. to the ton a second boiling in strong nitric acid should be given. If care be taken in using dilute acid at first and boiling gently, the gold will be left in one piece of a nearly black colour. The acid is now decanted off and the gold washed two or three times with distilled water. The gold may now be placed on an aluminium or other polished metal plate by inverting the capsule and leading the last drop of water and the gold with a glass rod on to the plate; the water is drawn off by a piece of filter paper and the plate gently heated till dry.

Having thus obtained the gold in a pure state, a bead is made with boracic acid on a platinum wire loop and pressed on the gold while still red hot. The gold adheres without difficulty, and by heating the bead before the blowpipe the gold is obtained as an almost perfect sphere. Should the resulting sphere of gold be very minute it is better to measure it under the microscope while in the bead, but if large enough to be seen with the naked eye it can be measured more accurately after dissolving the boracic acid bead in a watch-glass with hot water and placing the sphere of gold on a glass slide.

The plan of measuring minute prills of silver and gold to determine their weight was first introduced by Harkort, who used an ivory scale engraved with two fine lines meeting at an acute angle and divided into 50 equal parts. According to the fifth addition of Plattner's "Probirkunst," page 520, Goldschmidt determines the weight of silver and gold prills by measurement with the microscope. As I have not access to the paper on the subject his manner of preparing the prills for measurement is unknown to me. Harkort and Plattner, in making scales for the determination of the weight of gold and silver prills, weighed prills corresponding to the larger divisions of the scale, and from their weight calculated the weight for the smaller divisions. These prills were taken direct from the cupel, and at the point of contact are flattened; but as the amount of flattening is not always the same and hardly varies in extent with the size of the prill, and as the converging lines on the scale cannot be very sharply defined, this method is not capable of the same accuracy as where the almost perfect spheres are measured with the microscope.

* From the "Fifth Annual Report of the Council of the South Australian School of Mines and Industries, 1894."

TABLE I.

Assay Table, showing the Weight of a Sphere of Gold of one to fifty-hundredths of a millimetre in Diameter, and the Amount of Gold in ounces, pennyweights, and grains contained in a ton of Ore, &c., from the Diameter of the Sphere of Gold obtained in an Assay of 20 grms.

Diameter of Sphere in 100ths of a millimetre.	Corresponding weight of Gold Sphere in parts of a gramme.	20 grms. being taken for Assay, corresponding yield of Gold per ton. Ozs.	dwts.	grs.
1.	0·000,000,010,210,2	0	0	0·008,004
2.	0·000,000,08	0	0	0·064
3.	0·000,000,27	0	0	0·216
4.	0·000,000,65	0	0	0·512
5.	0·000,001,3	0	0	1·1
6.	0·000,002,2	0	0	1·728
7.	0·000,003,5	0	0	2·745
8.	0·000,005,2	0	0	4·098
9.	0·000,007,4	0	0	5·835
10.	0·000,010	0	0	8·004
11.	0·000,013	0	0	10·65
12.	0·000,017	0	0	13·83
13.	0·000,022	0	0	17·58
14.	0·000,028	0	0	21·96
15.	0·000,034	0	1	3
16.	0·000,042	0	1	8
17.	0·000,050	0	1	15
18.	0·000,059	0	1	22
19.	0·000,070	0	2	7
20.	0·000,082	0	2	16
21.	0·000,094	0	3	2
22.	0·000,101	0	3	13
23.	0·000,124	0	4	1
24.	0·000,141	0	4	14
25.	0·000,159	0	5	5
26.	0·000,178	0	5	20
27.	0·000,201	0	6	13
28.	0·000,224	0	7	7
29.	0·000,249	0	8	3
30.	0·000,276	0	9	0
31.	0·000,304	0	9	22
32.	0·000,334	0	10	21
33.	0·000,367	0	11	23
34.	0·000,401	0	13	2
35.	0·000,438	0	14	7
36.	0·000,476	0	15	13
37.	0·000,517	0	16	21
38.	0·000,560	0	18	7
39.	0·000,605	0	19	18
40.	0·000,653	1	1	8
41.	0·000,704	1	2	23
42.	0·000,756	1	4	17
43.	0·000,812	1	6	12
44.	0·000,869	1	8	9
45.	0·000,930	1	10	9
46.	0·000,994	1	12	11
47.	0·001,060	1	14	15
48.	0·001,129	1	16	21
49.	0·001,201	1	19	5
50.	0·001,276	2	1	16

No other flux seems to possess advantages equal to those of boracic acid for obtaining a sphere of gold. Borax and other fluxes are so fluid when hot that the gold is very liable to alloy with the platinum wire; this rarely occurs with boracic acid, on account of its great viscosity, even when white hot. Boracic acid is also easily soluble in water, so that the gold spheres can be separated without loss of time.

To test the accuracy of the tables and rules given further on a comparatively speaking large sphere of gold from an assay was measured and found to be 0·593 m.m., or $\frac{5}{8}$·$\frac{3}{4}$ m.m. in diameter, and $59{\cdot}3^3 \times 0{\cdot}000,000,010,210,2 = 0{\cdot}002,129$ of a grm. When weighed on a delicate assay balance it was found to weigh 0·0021 grm., and as this balance does not indicate beyond the fourth decimal the results may be considered identical. This sphere indicated gold in the sample tried at the rate of 30zs. 9dwts. 13grs. per ton. The smallest sphere of gold I have yet measured was from a blank litharge assay; it measured 0·024 m.m. in diameter, and by applying the rule given further on the weight would be $2{\cdot}4^3 \times 0{\cdot}000,000,010,210,2 \times 15{\cdot}432,35$ (to convert grammes to grains) = 0·000,002,178, or a little over two-millionths of a grain, or at the rate of $\frac{1}{3}$ gr. per ton.

Spheres of silver may be obtained and measured in a similar manner; the boracic acid acts slightly on the silver, but the quantity dissolved is inappreciable if the action is not prolonged. The sp. gr. of silver being 10·53 the weight of $\frac{1}{10^9}$ m.m. would be $0{\cdot}000,000,000,523,6 \times 10{\cdot}53 = 0{\cdot}000,000,005,513,508$ of a grm. In a test assay made with silver the sphere measured $0{\cdot}57 = \frac{57}{10^3}$ m.m., from which the weight deduced would be 0·001,02 gr., the balance showing the weight as 0·0010.

Copper, lead, and other metals cannot be melted in boracic acid on platinum wire without dissolving to a perceptible amount, but may with care be melted in sodic carbonate, and by dissolving the latter in hot water the sphere of copper, &c., obtained and measured.

The measurement of the spheres may be easily effected with a microscope magnifying about 100 diameters* by means of a micrometer eye piece and a test object plate ruled to hundredths of a millimetre or thousandths of an inch, the sliding tube carrying the eye piece being drawn out so that the eye piece lines coincide with the lines on the object glass. The object glass is, of course, only used for adjusting the eye piece. With microscopes having a graduated stage movement and an eye piece with crossed lines the measurement can also be effected.

NOTICES OF BOOKS.

Watts' Dictionary of Chemistry. Revised and entirely Re-written by M. M. Pattison Muir, M.A., Fellow and Prælector in Chemistry of Gonville and Caius College, Cambridge; and H. Forster Morley, M.A., D.Sc., Fellow of University College, London, and Lecturer on Physics and Chemistry at Charing Cross Hospital Medical School; assisted by Eminent Contributors. In Four Volumes. Vol. IV. with Addenda. London and New York: Longmans, Green, and Co. 1894. 8vo., pp. 922.

At last this new edition of the *magnum opus* is in the hands of the scientific public. We may fairly congratulate the editors on the able manner in which they have completed their gigantic task. So rapid is now the growth of chemistry that, although the editors and their colleagues have judiciously confined themselves to the pure science, leaving on one side its manifold applications, they are obliged to admit that "to give an account of what has been done in this department (organic chemistry) since the various volumes were published would occupy many hundred pages." It is highly probable that no further edition of this work will be undertaken, nor indeed any compilation in any other language, of a similar character. Hence we should advise our readers to secure copies whilst there is opportunity.

Among the most noteworthy articles in the present volume are that on phenyl and its compounds and derivatives, phosphorus and its compounds, especially the phosphines. The chemistry of photography has been ably handled by Prof. Meldola. Perhaps the most valuable article in this volume is "Physical Methods used in Chemistry," which exceeds 100 pp. in length, and includes, under the optical methods, the chemical applications of spectroscopy. This section will be inestimable to the spectroscopist as presenting a general view of the entire field. The portions on the infra-red and the ultra-violet on the harmonic relations between the spectral lines are very suggestive. Much as has been done in these directions, we cannot help feeling how much remains undone. We find here a bibliography of the principal works and memoirs on spectroscopy.

Under the head "Optical Methods" we find also an elaborate paper on the "Rotation of the Plane of Polarisation of Light." This subject has been much more clearly studied in France and Germany than in England, and its development, especially with reference to the analyses of sugars, has been no small part of the operations by which our sugar-trade has been so severely damaged. But the purely scientific importance of polarimetry is shown by the light which it throws on the constitution of a number of organic compounds.

Rotatory polarisation is further brought into co-relation with magnetism and with electricity.

The chemical action of diffusion and dialysis are duly noticed. It is pointed out that Graham's views on the nature of colloids have been confirmed by the more recent researches of Van Bemmelen.

Electrical methods occupy a much larger share of the attention of the editors. The rise and fall of the electro-chemical theory of Berzelius is expounded. The law of Faraday is shown to connect itself with the most advanced chemical views of the present day.

As regards the origin of electromotive force, we have still the undecided issue between the contact theory and the chemical theory. The section on "Electrical Methods" will, however, supply the student with a very satisfactory view of the border-land between chemistry and electricity.

Amongst other articles of value we must mention those on platinum, rhodium. vanadium, ruthenium, tantalum, titanum, and tungsten.

As a work of reference—which is distinctly its object—the new edition of Watts is unrivalled in the English langnage, or, to the best of our knowledge, in any other.

A Text-Book of Inorganic Chemistry. By G. S. Newth, F.I.C., F.C.S., Demonstrator in the Royal College of Science, London, and Assistant-Examiner in Chemistry, Science and Art Department. London and New York: Longmans, Green, and Co. Crown 8vo., pp. 667. 1894.

The work before us holds an intermediate place in its numerous tribe. As regards the facts which form its subject-matter it presents, of course, nothing novel. The arrangement, however, is rather peculiar. Mr. Newth still recognises the old division of the elements into metals and non-metals, and even tolerates the unhappy term "metalloids."

The first part, entitled "Introductory Outlines," is very ably written. The chapters on dissociation, on electrolysis, on the periodic system, and on thermo-chemistry, deserve to be thoughtfully read over by the student, the

* I find that a Zeiss microscope with No. 3 micrometer eye-piece and B objective, and with the eye-piece sliding tube fully pulled out, gives exactly the desired magnification for 1/100th of a millimetre.

rather as we still find writers and speakers who, *e.g.*, do not distinguish between dissociation and decomposition. As a matter of course the author accepts the periodic classification; but, as it has "not been generally adopted as the basis of elementary English text-books," he attempts a compromise.

To this end, in Part II., he discusses "the four typical elements," hydrogen, oxygen, nitrogen, and carbon, and their more important compounds. Then, and then only, in Part III., he takes up the elements systematically according to the periodic system. Whether, by thus doing homage to "the prevailing methods of instruction," he has facilitated the study of chemical Science, is, to say the least, a very open question.

The rare elements, it will be perceived, are omitted. The author acknowledges, indeed, that many of them are of the greatest interest and importance; but he pleads that "they stand quite outside the range of all the customary courses of chemical instruction." If so, surely these courses and those who prescribe them are much to blame. Further, he urges that books of reference "are frequently *uncut* in those portions which treat of the elements." But why is this the case? Plainly because those students whose object is rather to "pass" than to "know" find no occasion to refer to these portions!

If we could except the peculiar arrangement of this book, and the omission of some of the rarer elements, we should pronounce this work deserving of almost unqualified approbation.

Laboratory Manual of Elementary Physiology, and Urine Analysis. By John H. Long, M.S., Sc.D., Professor of Chemistry and Director of the Chemical Laboratories in the Schools of Medicine and Pharmacy of Northwestern University. Chicago: E. H. Colegrove and Co. 1894. Pp. 366.

The author of this manual complains—with, we fear, good causes—that the time given to the study of chemistry and chemical physiology in American medical colleges is altogether too short. Hence the chemical attainments of the graduates fall short of the standard which may reasonably be expected.

In the text we find nothing to which exception may be fairly taken. In the determination of chlorine in waters we notice that the author uses, as an indicator solution of neutral potassium chromate. We have always been accustomed to use this salt in the solid state, taking about 30 m.grms. As indicators in alkalimetry and acidmetry the author uses litmus, cochineal, phenolphthalein, methyl-orange, and rosalic acid.

The reader must bear in mind that the American measures for liquids here given are not identical with those used in Britain; for instance, our fluid oz. is not 1-16th but 1-20th of a pint.

In speaking of sugars, the author describes the polarisation process at some length, and figures the necessary apparatus. The use of the spectroscope in the examination of blood is also described, but the lettering to the figure (fig. 31) is nowhere explained. This is of the less importance as figures of spectroscopes are common in chemical and physical works, and in the catalogues of dealers. The spectro-photometer is also described and figured. The special tests required in the analysis of blood, biliary fluids, and urine, are fairly described.

As a whole the book must be recommended to students preparing for a medical career, or entering upon physiological research.

A Laboratory Guide and Analytical Tables for the Use of Junior Students. By James Grant, F.I.C., F.C.S., Chief Assistant-Lecturer and Demonstrator of Chemistry at the Municipal Technical School, Manchester. Manchester: Smith and Wood. 1894. 8vo., pp. 49.

"What; will the line stretch out to the crack of doom? Another yet?"

We have repeatedly been led to question the *raison d'être* of a series of books, all containing the same subject-matter, and differing merely in language and in details of arrangement. We have even ventured to suggest that pending the avatar of some capital discovery, such, *e.g.*, as the decomposition of one of our reputed elements, it might be well to refrain from the issue of more manuals, text-books, handbooks, and guide-books. Our remonstrances have been in vain. The issue of new elementary treatises on chemistry seems to depend not so much on the appearance of some great discovery as on the promulgation of a new South Kensington Syllabus.

In the work before us we certainly find nothing erroneous, but neither do we see any marked advantage over other elementary treatises.

Our Secret Friends and Foes. By Percy Faraday Frankland, Ph.D., B.Sc., F.R.S., F.C.S., &c., Professor of Chemistry in Mason College, Birmingham. A New Edition, Revised, with Additions. London: Society for Promoting Christian Knowledge. New York: E. and J. B. Young and Co. 1894. Post 8vo.

We can heartily welcome the appearance of the work before us. Bacteria, if sometimes too numerous in our air or water, are almost as rife in our political and literary Journals and our sensational novels. There the micro-organisms are made to figure in guise alarming to the outside world and supremely ridiculous to men of Science. Prof. P. F. Frankland deserves, therefore, public gratitude for describing some of the most important of these tiny beings in language "understanded of the people," and at the same time in full accord with the most recent results of Science.

After an Introduction in which the general forms of micro organisms are described and illustrated, the author proceeds to a fuller notice of the micro-organisms in air—with an account of the controversy on spontaneous generation and of the antiseptic treatment of wounds—and in water. It is shown that although the mature bacilli and spirilla, as a rule, do not grow and multiply in drinking-water, yet their spores persist even in the purest waters.

The next chapter treats of useful micro-organisms, among which the place of honour belongs to those beings which enable certain vegetables, especially peas, beans, and lentils, to condense and utilise the free nitrogen of the atmosphere, and thus keep up the fertility of the soil. Those which effect the transformation of ammonia into nitric acid are also not forgotten. Here, we submit some mention might have been made of the experiments of Georges Ville.

One micro-organism here characterised as useful, the *Saccharomyces cerevisiæ*, will be regarded with different feelings by the so-called "Temperance" party, who without it would have to seek something else to denounce.

Among malignant micro-organisms our attention is especially drawn to the bacilli of anthrax (wool-sorter's disease), of tuberculosis, of tetanus and typhoid fever, and the spirilla of cholera. Prof. Frankland truly says that in preventive medicine we have in England unfortunately lagged behind. This disgraceful position is due in great part to the "anti-party." We fear that our author is too sanguine when he expresses a hope that public opinion is "beginning to appreciate the importance of such beneficent investigations." Certainly his work will do much to convince rational persons, but the true "anti" orator or writer is born irrational, and we believe never recovers from his delusions.

We only hope that the lessons of Metchnikoff and Kitasato may not be studied and applied in the wrong way.

The last chapter of this most interesting work discusses the action of light on micro-organisms. One practical

conclusion to be drawn from the facts here shown is that all tanks and beds for the treatment of sewage, &c., should be as much as possible exposed to the light. Precipitation-tanks roofed over, whether at Crossness or elsewhere, are a grievous mistake.

Whilst thus endeavouring to bestow upon Prof. Frankland our meed of applause and encouragement, we must also award the highest encomium to the Society for Promoting Christian Knowledge. They have refused to bow down to the dictates of aggressive ignorance, and have shown that there is no hostility, or cause for hostility, between Science and an enlightened Christianity.

The Rasa-Ranga-Rahasya. The First and only Indian Organ of the Chemical and Dyeing Trades. Vol. I., No. 1.

THIS latest addition to chemical literature points forcibly to the wonderful progress that has been made in India of late years. The new Journal (a monthly one) is edited by Messrs. Deshmukh and Gajjar, and, being printed almost entirely in one of the native dialects, shows that they expect sufficient support among the scientific Indians to make it a financial success. We offer the enterprising founders our hearty congratulations, and wish them a long and successful career.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxix., No. 14, October 1, 1894.

Action of Hydrogen Phosphide upon Potassammonium and Sodammonium.—A. Joannis.—If hydrogen phosphide is passed into potassium dissolved in liquefied ammonia, the hydrogen phosphide disappears by degrees and hydrogen is evolved. In the tube there is formed a liquid which does not mix with the ammoniacal solution, but which dissolves a small quantity of the latter. Ultimately there are formed fine white needles of the composition PH_2K, analogous to potassium amidide, NH_2K. With sodammonium the ultimate product is a white solid body, soiled with a little yellow phosphide.

Researches on Mercuric Picrate.—Raoul Varet.—On comparing the author's results with those of Berthelot for the mercuric acetate, chloride, and cyanide, we see that the picrate ranks along with the acetate; the neutralisation heat with HgO evolves + 6·0 cal. Whilst picric acid opposed to hydrocyanic acid in presence of potassa displaces it in the solution without precipitation, whilst + 10·7 cal. of heat are evolved in presence of mercury oxide, hydrocyanic acid completely displaces picric acid, evolving + 12·2 cal. for each mol. of the two acids.

Action of Picric Acid and Picrates upon Metallic Cyanates. The Isopurpurates.—In the action of picric acid and picrates upon the metallic cyanides there is a formation of isopurpurates whenever the picric acid displaces the hydrocyanic acid from the cyanide, whilst this formation does not take place when the hydrocyanic acid displaces the picric acid. The author has verified this reaction in the case of many metals.

Antiseptic Properties of the Vapours of Formal (Formic Aldehyd).—A. Trillat.—The author proves that the vapours of formal kill *Bacillus anthracis*, Eberth's bacillus, the *Bacillus coli*, &c.

Observations on Flours.—M. Balland.—After examining 250,000 samples of flour in the laboratory of the War Department from September, 1891, to June, 1894, the author finds that the highest proportion of water is 16·20 per cent, and the lowest 9·40 per cent. The maximum of moist gluten was 47·5 per cent; the maximum of fatty matter 3·10 per cent; the minimum of acidity 0·013 per cent.

Zeitschrift für Anorganische Chemie,
Vol. vii., Parts 1 and 2, August 4, 1894.

Fluoplumbates and Free Fluorine. — Bohuslav Brauner.—This paper cannot be completely abridged without the two accompanying figures. The author concludes with the remark, that the more tetravalent lead is studied the more resemblance it shows to tetravalent tin. He hopes that a study of the tin tetrafluoride liberated from the fluostannates by sulphuric in comparison with lead tetrafluoride will throw further light on both these substances. At present the study of the compounds above described is a further proof in favour of the insertion of lead in the fourth group of the system of Mendeleeff. Thirty years ago it could scarcely have been predicted that lead could form compounds analogous on the one hand to those of tin, and on the other to those of carbon, silicon, cerium, and thorium. The author considers that free fluorine in 96 mols. F_2 contains 8 atoms F_1.

Detection of Alkaline Perchlorates in presence of Chlorides, Chlorates, and Nitrates.—F. A. Gooch and D. A. Kreider.—Already inserted.

Production of Chlorine for Laboratory Purposes.—F. A. Gooch and D. A. Kreider.—Already inserted.

Action of Gaseous Hydrochioric Acid upon Sodium Vanadiate.—E. F. Smith and Jos. G. Hibbs.—The authors ascertain that it is possible to eliminate vanadic acid from its salts by exposure to a current of gaseous hydrochloric acid at temperatures between that of a dwelling-room and 440°.

Reaction of Molybdic Acid with Potassium Mono- and Di-Chromate.—R. H. Bradbury.—The reaction between molybdic anhydride and potassium chromate takes place according to the equation—

$$2K_2CrO_4 + MoO_3 = K_2Cr_2O_7 + K_2MoO_4.$$

No chromomolybdic compound is formed. Molybdic anhydride does not appear to react with potassium dichromate in the cold, but at high temperatures there is formed a basic potassium chromium molybdate—

$$K_2O.Cr_2O_3.3MoO_3.$$

Action of Molybdenum Dioxide upon Salts of Silver.—E. F. Smith and O. L. Shinn.—Brown molybdenum dioxide (as well as metallic molybdenum) precipitate metallic silver from a slightly ammoniacal solution of silver nitrate. The authors direct attention to the further analogy between molybdenum dioxide and the dioxides of other metals of Group VI.

On Atmospheric Ozone.—Em. Schöne.—The author points out two errors in a former paper. The minimum of atmospheric ozone is in *July*, and not in *June*. It is also stated that "during thunderstorms and heavy showers the spectroscope *never* shows the presence of ozone." It should be *only* shows, &c.

On Prof. Spring's Claim of Priority.—M. Carey Lea.

Reply to the above Communication.—W. Spring.—A claim of priority as regards the conversion of mechanical into chemical energy.

The State of Solution of Iodine, and the Probable Cause of the Difference of Colours in its Solutions.—G. Krüss and E. Thiele.—This very interesting paper cannot be usefully abridged without the insertion of the two figures and the numerous tables.

Use of Mercuric Oxide in Analysis.—E. F. Smith and P. Heyl.—(See p. 192).

Journal fur Praktische Chemie.
New Series, Vol. l., Parts 3, 4, and 5, 1894.

Researches from the Laboratory of A. Weddige.—These consist of a paper, by C. Brock, on tribromacetonitril, and on some derivatives of polymeric trichloracetonitril.

Studies on Tautomerism. — W. Brühl. — This memoir, which runs to more than 100 pages, discusses the collocation of the material to be observed, according to its source and its mode of preparation, the isomerism of position, the isomerism of saturation, the true ketones and diketones, the ketonic acids, the keto-forms of acetacetic esters and its derivatives, pseudo forms (enolic forms) among the derivatives of acet-acetic esters, other pseudo keto-derivatives (enolic compounds) of acetic ester (oxalacetic ester); the esters of succinic, methylsuccinic, and malonic acids; the acetylised esters of malonic and ethylmalonic acids, the pseudo ketones, the keto-derivatives of acetone, the pseudo forms (enolic compounds) of acetone; the oxymethylen compounds (aliphatic); the oxymethylen compounds of camphor; the camphor-carbonic acid derivatives; pyrotartaric acid.

The Molecular Weight of Mercurous Chloride.—M. Piloth.—The author, referring to a recent paper by Harris and V. Meyer, in No. 11 of the *Berichte*, rejects the formula, Hg_2Cl_2, proposed for calomel, as in that case the vapour-density should be much nearer 16·28 than 8·16, as actually obtained.

A New Synthesis of Phenol Alcohols.—L. Lederer.—The author holds that if the tendency of the phenol alcohols is taken into account, it becomes easy to obtain phenol alcohols by the apposition of formaldehyd to the phenols.

Pyrazolon and Isopyrazolon. — R. von Rothenburg.—The pyrazolons and isopyrozalons are tautomeric and isomeric only in their derivatives. The author contests the view of S. Ruhemann, who believes that he has isolated isopyrazolon.

On Phenylisoxazolonimid. — R. von Rothenburg.—The author admits that the constitution of this compound has been previously given by P. S. Burns, whose priority he admits.

Researches from the Laboratory of the University of Freiburg.—These researches comprise a paper by Ad. Claus and H. Howitz on β-bromquinolin and γ-bromquinolin, and a note by Ad. Claus on the two isomeric forms oi diazobenzol potassium sulphite.

Revue Universelle des Mines et de la Metallurgie.
Vol. xxvii., No. 1.

Notice on the Use of the Blum Apparatus for the Absorption and the Oxidation of Sulphuretted Hydrogen.—This paper is a description of the apparatus as here figured. To ascertain whether the vapours escaping carry away any sulphuretted hydrogen they are caused to pass over a tissue steeped in cadmium acetate, which would be at once turned of a yellow colour. The oxidation is effected either by means of a saturated solution of bromine in hydrochloric acid or by means of ammoniacal hydrogen peroxide.

MISCELLANEOUS.

Disease-Germs in Bread.—At the late meeting of the British Medical Association it was shown that bread is not sterilised by the heat to which it has been subjected in the baker's oven. The average temperature in the centre of a quartern loaf does not exceed 186° F., and in a half-quartern loaf 203° F. An eminent medical contemporary justly observes that this fact is a weighty reason for the improvement of the sanitary condition of bakeries.

MEETINGS FOR THE WEEK.

FRIDAY, 26th.—Physical 5. (At the Rooms of the Chemical Society, Burlington House). "On the Thermal Constants of Aniline," by Mr. Griffiths. A Voltameter by Mr. Naber will be on view.

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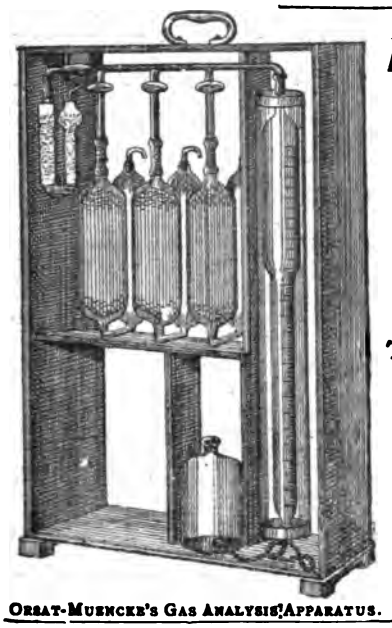

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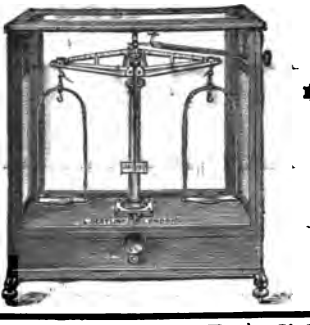

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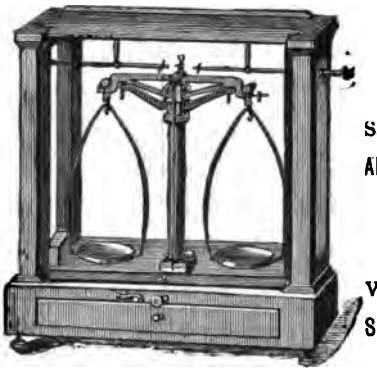

FIG. 3a.

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THE CHEMICAL NEWS.

Vol. LXX., No. 1822.

STRUCTURE OF GOLD NUGGETS.*

(Abstract of Preliminary Note).

By Professor A. LIVERSIDGE, M.A., F.R.S.

Gold nuggets, on being cut through, or sliced and polished, and then etched by chlorine water, were found to exhibit well-marked crystalline structure, closely resembling the Widmanstatt figures shown by most metallic meteorites, except that, in the nuggets, the crystals are more or less square in section and show faces which evidently belong to the octahedron and cube.

On heating the nuggets in a Bunsen burner, blebs or blisters form, on both the polished and unpolished surfaces; and on still more strongly heating, these, in some cases, burst with sharp reports, and pieces of gold are projected with considerable violence.

As no explosions have been observed on dissolving or eating away the crusts of these blisters by chlorine water, it would appear that the blebs are probably due to the vapourisation of some liquid or solid substance.

As soon as a fresh supply of nuggets is obtained, experiments will be proceeded with to ascertain definitely whether gold nuggets contain occluded gases, or liquids or solids which are vapourisable.

In slicing some nuggets, scattered granules of quartz were met with inside, although quite invisible outside, and at first it was thought that the explosions might be due to the quartz; but the gas, in some cases, continued to issue from the burst bleb (where the aperture formed was small), and forced the Bunsen flame out into lateral jets, just as if urged by a blowpipe.

THE PRESENCE OF VANADIUM IN COMMERCIAL CAUSTIC SODA.

By H. L. ROBINSON.

Whilst saturating a solution of caustic soda with washed hydrogen sulphide, it was noticed that after some time the liquid became of a deep purple colour. As there could be little doubt that this was due to the presence of some impurity, it appeared to be of interest to investigate the matter.

When the liquid saturated with hydrogen sulphide was exposed in a good light, with access of air, its colour faded slowly, and the liquid became yellowish, a brown substance being deposited at the same time.

Some of the brown deposit was collected, washed, and dissolved in aqua regia; excess of pure sodic hydrate was next added, and hydrogen sulphide passed to saturation. A purple-coloured liquid was the result.

Some of the same sample was dissolved in water; sulphuretted hydrogen was passed, as before, till a brownish-purple-coloured liquid was obtained; it was then filtered through glass-wool, and rendered slightly acid with hydrochloric acid. The brown precipitate, on ignition, gave a brown, fusible, crystalline mass, soluble in acids or alkalis, which, with sodic carbonate and potassic nitrate, yielded a vanadate.

Some of the same soda solution was taken, and hydrogen sulphide passed till it became purple; and a solution of pure soda, to which a small quantity of sodic vanadate had been previously added, was treated in precisely the same manner. The two solutions, when examined with the spectroscope, gave identical absorption spectra, which, as the colour of the solutions faded, changed in a similar manner. This made it certain that vanadium was present in the soda.

In order to ascertain whether the vanadium was present as a vanadate, a solution of the soda was acidified with sulphuric acid and hydrogen peroxide, but no colouration was produced.

Of the materials used in the manufacture of commercial caustic soda, common salt, sulphuric acid, limestone, coal, and sodium nitrate, the only one from which the vanadium could possibly be derived is the coal.

Although it is well known that vanadium frequently occurs in iron ores, I have been unable to find any reference to its having deen detected in coal.

To estimate the amount of vanadium present, 100 grms. of the caustic soda were dissolved in water, and hydrogen sulphide passed till the solution became brownish-purple; it was then filtered, allowed to stand, and slight excess of hydrochloric acid added. The brown precipitate, after being collected on a filter and washed till the washings no longer gave a precipitate with silver nitrate, was dried and ignited in a weighed platinum dish. The 100 grms. of soda gave 0·0376 grm. of V_2O_5, or 0·0211 grm. of vanadium.

It was found that when a vanadate was present in a solution of soda in far smaller proportion than this, it gave a distinct colouration with hydrogen peroxide. It would seem therefore that the vanadium is not present in the soda as a sodium vanadate.

The vanadic oxide obtained was fused with about four times its weight of sodic carbonate, a little potass nitrate added, and the whole fused again; the mass was then dissolved in water, and the solution tested in the usual way for a vanadate.

Chemical Laboratory, Guy's Hospital.

ON A PTOMAINE EXTRACTED FROM URINE OF PATIENTS SUFFERING FROM PLEURISY.

By A. B. GRIFFITHS, Ph.D., F.R.S.E., &c.,
Lecturer on Chemistry at the Central School of Chemistry and Pharmacy.

The word "ptomaine" (from Greek *ptoma*) is no longer restricted to the substances derived from decomposing animal tissues, as ptomaines have been found in the excretions of the body during life, especially in pathological states; and it has been shown that diseases can be communicated by these substances in the entire absence of microbes. Gautier calls the substances produced in the system during life *leucomaines*, while he reserves the word ptomaine for those substances formed by putrefaction after death. But does it follow that the terms ptomaines and leucomaines should be considered as absolutely distinct? In the present state of our knowledge of these curious substances, this is not admissible. It is often in vain to try to trace rigorously where one series of "alkaloids" begins or the other terminates. In fact, it is extremely difficult, if not impossible, to draw the limits of the word ptomaine. As a rule the ptomaines are allied to the vegetable alkaloids; the majority of them contain carbon, hydrogen, nitrogen, and oxygen; some are, however, devoid of oxygen; and the ptomaine (or toxine, as Brieger would call it) to be described in this paper does not contain nitrogen. Many ptomaines have been isolated from urine in cases of infectious and other diseases (Luff, in *British Medical Journal*, July 27, 1889; Hunter, in *British Medical Journal*, July 12, 1890; and Griffiths, in *Comptes Rendus de l'Académie des Sciences*, Paris, tomes cxiii.-cxviii., and Griffiths's "Manual of Bacteriology," Heinemann); and a few of the same

* Read before the Royal Society of N.S.W., Sept. 5th, 1894.

ptomaïnes have been isolated from pure cultures of certain pathogenic microbes (Brieger, in *Berliner klin. Wochenschrift*, 1888; *Virchow's Archiv.*, 1887-9; *Berichte*, xix., 3119; Griffiths, in *Comptes Rendus de l'Académie des Sciences*, Paris, t. cxiii., p. 656, t. cxiv., p. 496, p. 1382, *Bulletins de l'Académie Royale de Belgique*, 3 e. s., t. xxiii., p. 840, and Griffiths's "Researches on Micro-Organisms," Baillière).

The ptomaïne described in this paper was extracted from urine of patients suffering from pleurisy, by the following method:—(*a*) A large quantity of urine was made alkaline by the addition of sodium carbonate, and then agitated with half its volume of ether. (*b*) The ethereal solution (after standing) was filtered and agitated with a solution of tartaric acid. The tartaric acid combines with any ptomaïne present, forming a soluble tartrate, and the tartrate solution forms the lower layer of the liquid. (*c*) The tartaric acid solution (after being separated from the ether) was also made alkaline by the addition of sodium carbonate, and was once more agitated with half its volume of ether. (*d*) The ethereal solution (after standing) was separated, and the ether allowed to evaporate spontaneously. (*e*) The residue (after drying over sulphuric acid) was treated with water, an excess of pure calcium hydroxide added, and the mixture evaporated on a water-bath. The residue so obtained was treated with chloroform and filtered. The filtrate (after evaporation) yielded the ptomaine in an isolated and a crystalline condition.

This ptomaïne (which may be called "*pleuricine*") is a white crystalline substance, with a slight hawthorn-like odour. It is readily soluble in hot water, and on cooling the solution deposits beautiful feathery crystals. Concerning these crystals, Mr. W. J. Pope, F.C.S. (of the City and Guilds Central Technical College, South Kensington), who kindly investigated them for me, gives the following description:—"On slowly cooling the hot, concentrated, aqueous solution, the substance separates in aggregates of colourless, transparent, rectangular plates, possessing a calcite-like lustre. The crystals belong to one of the biaxial systems, and one of the optic axes emerges normally to the large faces of the plates. The extinction is straight, the double refraction strong, and the dispersion considerable." I may say, *en passant*, that I had not sufficient material for Mr. Pope to obtain the substance in measurable crystals, but he says that the foregoing qualitative description "is quite sufficient for the identification of the substance, and he can undertake to prove the identity of this ptomaïne with any other product at any future time."

This ptomaïne is precipitated by hydrochloric acid, after standing some time, as a white crystalline hydrochloride. Nessler's reagent gives with it a pale yellow precipitate; and after standing some time the precipitate darkens and becomes brownish, the liquid appearing pinkish by transmitted light. The precipitate, on heating, is destroyed or re-dissolved, and the solution becomes colourless. Potassium ferrocyanide gives no precipitate at first, but on warming the mixture a white or pale yellow precipitate is produced, and after standing some time it becomes of a greenish hue. Ferric chloride gives a white precipitate with this ptomaïne. Potassium-cadmium iodide (Marmé's test) gives a red precipitate; potassium-bismuth iodide (Dragendorff's test) produces a green precipitate; and phosphoantimonic acid gives a bluish precipitate. Phosphotungstic acid, after standing with the ptomaïne solution for some time, throws down a white crystalline precipitate.

The following figures were obtained on the analysis of the ptomaïne:—

0·1580 grm. of substance gave 0·3328 grm. of CO_2 and 0·0724 grm. of H_2O.

	Found.	Calculated for $C_5H_5O_2$.
Carbon	57·44	61·79
Hydrogen	5·09	5·16
Oxygen	—	33·05

From the foregoing percentage composition, $C_5H_5O_2$ represents the formula of this new ptomaïne. It is a poisonous substance, which readily kills mice and other small animals. It does not occur in normal urine; it is, therefore, produced within the body during the course of the disease (pleurisy).

In conclusion, I wish to take this opportunity of expressing my indebtedness to Messrs. W. J. Pope, F.C.S., W. L. Gadd, F.I.C., and E. A. Wagstaffe, Ph.D., B.Sc. (Vict.), who helped me with some of the work recorded in this paper.

CONTRIBUTIONS TO THE CHEMISTRY OF CERIUM.*

By L. M. DENNIS and W. H. MAGEE.

The mineral cerite was first found in one of the iron mines of Bastnäs, in Westmanland, Sweden. Its peculiarity was noticed as early as 1751 by Cronstedt (*Sv. Vet. Akad. Handl.*, 1751, S. 227), and in 1784 it was analysed by d'Elhuyar (*Sv. Vet. Akad. Handl.*, 1784, S. 121), in Bergmann's laboratory, and was considered by these two chemists to be a silicate of lime and iron. In 1803 the mineral was again examined by Berzelius and Hisinger, and by Klaproth, and nearly at the same time, but independently, they discovered in the mineral a new oxide. Berzelius and Hisinger named the earth *ceria* (*Afhandl. i. Fysik. Kemi och Mineral.*, i., 58) after the planet Ceres, which had been discovered two years before by Piazzi. Klaproth called it *ochroiterde* (*A. Gehl.*, ii., 303; *Beiträge*, iv., 140), from its brownish yellow colour. Fortunately the former name was adopted, for the latter name would have been a misnomer, since pure cerium dioxide as we now know it has a pale yellow colour.

From that time to the present, cerium and its compounds have frequently been the subject of investigation, but the work of the earlier chemists is not of direct importance, since the ceria upon which they worked was, as we now know, a mixture of various oxides, chief among them being those of cerium, lanthanum, and didymium.

In 1839, however, Mosander made known a discovery of the highest importance; namely, that ceria was not a simple oxide, but a mixture of at least two. The newly isolated earth he called *lanthana*, and this, in 1842, he split up into lanthana proper, and another oxide which he named *didymia* (*Förh. Skand. Naturf. Stockholm*, 1842, 387; *Phil. Mag.*, xxviii., 241; *Pogg. Ann.*, lvi., 503; *J. Prakt. Chem.*, xxx., 276).

Dating from the time of Mosander's discoveries, the results of the various investigations upon cerium acquire, of course, much greater value, but the chemistry of this element and the other rare earths has remained one of the most difficult problems in the field of inorganic chemistry, chiefly because of the great similarity in the chemical behaviour of these different elements and the consequent difficulty of separating any one of them completely from the others. Naturally, then, in an experimental investigation of the compounds of cerium, the first problem to be solved is the preparation of pure ceria.

I.—*Separation of Ceria from the other Earths.*

The ceria was extracted from allanite from Amelia County, Virginia, a large amount of this mineral having been most kindly sent to us by Professor W. G. Brown, of the Washington and Lee University.

1924 grms. of the finely powdered allanite were heated in large porcelain evaporators with concentrated hydrochloric acid until the supernatant liquid became dark brown. The syrupy liquid was allowed to cool and was then poured off, the residual mineral being again treated

* From the *Journal of the American Chemical Society*, October, 1894. Read at the Brooklyn Meeting, August 15, 1894.

in the same manner until it became greyish white, three treatments of about ten hours each usually sufficing. A portion of the residue was then moistened with concentrated sulphuric acid and heated until all of the acid was driven off. The white residue was thrown, in small portions at a time, into ice-water, and to the filtered solution oxalic acid was added. No precipitate resulted, showing that the treatment with hydrochloric acid had removed all of the rare earths.

The rare earth chlorides, mixed with those of iron, aluminium, calcium, &c., were then diluted and filtered. A portion of this filtrate was treated with hydrogen sulphide for twenty-four hours, the solution being kept at 70°, but no precipitate appeared. The hydrogen sulphide was then expelled by boiling, the sulphur was filtered off, and the filtrate was added to the original solution. This was oxidised by nitric acid and a concentrated solution of oxalic acid was then added in excess. The pinkish white precipitate of the rare earth oxalate was allowed to settle, and the oxalates were then washed by decantation with hot water until the supernatant liquid was colourless. They were then digested in large evaporators with 1 per cent hydrochloric acid until all iron had been removed, and were then dried and ignited in a muffle furnace. The reddish brown oxides resulting weighed 410 grms., a yield of over 21 per cent.

The oxides were dissolved in concentrated nitric acid. To facilitate solution, sulphurous acid was added to one portion and oxalic acid to another, but with no perceptible benefit in either case. There were obtained 4 litres of an almost syrupy solution which showed the didymium absorption bands very strongly.

Many different methods for separating the ceria from the accompanying earths have been proposed, but none of them seem to yield cerium which is completely free from lanthanum and didymium, unless the method proposed be many times repeated. Mosander (*Phil. Mag.*, xxviii., 241), the earliest worker upon this problem, obtained a mixture of didymia and lanthana, free from ceria, by precipitating the mixed chlorides with potassium or sodium hydroxide, and passing chlorine through the suspended hydroxides. Cerous hydroxide is oxidised to the insoluble ceric hydroxide, while the hydroxides of lanthanum and didymium are changed to chlorides and dissolve. Jolin (*Bihang till K. Sv. Vet. Akad. Handl.*, ii., 14; *Bull. Soc. Chim.*, [2], xxi., 533) found that the treatment must be made seven times before the ceria is completely free from didymia and lanthana. Popp (*Ann.*, cxxxi., 359; *J. B.*, 1864, 195 and 702) added sodium acetate to the solution of the chlorides and ran in chlorine, the cerium being precipitated. Later, instead of passing in chlorine gas, he added sodium hypochlorite and boiled. Gibbs (*Sill. Amer. Journ.*, [2], xxxvii., 332) boiled the mixed earths with nitric acid (1 : 2) having first added considerable lead dioxide. Zschiesche (*Journ. Prakt. Chem.*, cvii., 65) heated the rare earth sulphates with red lead and nitric acid. In each of the last two methods ceric oxide is formed. Winkler (*Journ. Prakt. Chem.*, xcv., 410) separated ceria and didymia from lanthana by adding mercurous oxide to the solution of the chlorides, and then potassium permanganate until the solution is coloured by the latter. Ceria and didymia are precipitated. Welsbach (*Monatsh. f. Chem.*, iv., 630) precipitates the ceria by fractional crystallisation as cerium ammonium nitrate. Bunsen first (*Ann.*, cv., 40) proposed to ignite the oxides with magnesia, to dissolve out the ceria as cerium-magnesium nitrate, and then pour the solution of the latter into a large amount of very dilute nitric acid, whereby ceric oxide is precipitated. Later (*Pogg. Ann.*, clv., 375) he abandoned this method and proposed instead the method which has been most employed for preparing pure ceria. A solution of impure cerium sulphate is poured into boiling water containing one part of nitric acid to the thousand, and basic cerium sulphate is thrown down. This procedure must be repeated several times, and is also very wasteful because the yield is small, so that it can be used with advantage only on material that is already nearly pure. Brauner (*Monatsh. f. Chem.*, vi., 792) increased the yield by dissolving finally in nitric acid instead of in sulphuric acid, driving off the excess of acid and precipitating with boiling water containing nitric acid. Debray (*Compt. Rend.*, xcvi., 828) fused the nitrates of the earths with from eight to ten times their weight of potassium nitrate at a temperature between 300° and 350°. The nitrate of cerium is decomposed, leaving the oxide, which is insoluble in water. The other nitrates are undecomposed and are soluble in water. Many repetitions were necessary to free the ceria from the other earths. Pattinson and Clark (Chem. News, xvi., 259) heated the mixed chromates to 110° when cerium chromate decomposes to ceric oxide, the other chromates remaining unchanged.

For the separation of the ceria from the other earths in the allanite solution obtained as stated above, the authors first employed the Mosander-Jolin method, which so eminent an investigator as Cleve has pronounced to be the best. The nitrate solution of the earths was diluted, potassium hydroxide was added in excess, and well-washed chlorine gas was run into the solution for from four to five days. The white precipitate of the hydroxides soon changed to a dirty violet, and became light yellow soon after the action of the chlorine began. The ceric oxide was washed by decantation until the wash-water gave no precipitate with ammonium hydroxide, this washing occupying nearly a week, as the precipitate settles very slowly. The precipitate was then dissolved in hydrochloric acid, and the treatment with chlorine was repeated. After seven complete treatments the concentrated solution of cerium chloride showed no absorption bands when a layer 10 c.m. thick was examined with a Krüss spectroscope. The solution was then nearly neutralised with ammonium hydroxide, and hydrogen sulphide was run in for twenty-four hours, the solution being warmed to 70°. A very slight precipitate of copper sulphide resulted. This was filtered off, the hydrogen sulphide was expelled by boiling, and the separated sulphur was removed by filtration. To the filtrate was added a concentrated solution of pure oxalic acid, a snow-white precipitate of the oxalates of the rare earths resulting. This precipitate was treated with a hot solution of hydrochloric acid (2 per cent) until the washing liquid failed to give a reaction for iron when tested with potassium sulphocyanate and ether, The oxalate was then dried and ignited in porcelain crucibles over the blast-lamp. The resulting oxide was of a pale yellow colour, resembling in tint very light chamois leather.

In the meantime the method of separation proposed by Debray was tried upon another portion of the rare earths. It was found that the melting-point of the mixture of rare earth nitrates and potassium nitrate was usually about 325°. (The melting-point of potassium nitrate is stated to be 339°). Upon treating the fused mass with water it was found that the insoluble residue contained, even after two fusions, appreciable amounts of didymium. Since cerium nitrate begins to decompose at 200° and didymium nitrate at about 300°, the cause of the presence of didymium in the insoluble cerium oxide is evidently to be ascribed to the high melting-point of the nitrate mixture employed by Debray. If, then, the melting-point of the mixture could be lowered, the probable result would be that less of the didymium nitrate would be decomposed, and it seemed reasonable to expect that, by sufficiently depressing the melting-point, cerium oxide completely free from didymium might be obtained by a single fusion. With this end in view the potassium nitrate was replaced by sodium nitrate, the melting-point of the latter, 316°, being somewhat lower than that of the potassium nitrate. But even with this salt more than two fusions were necessary to free the cerium from didymium.

Carnelley and Thomson (*Journ. Chem. Soc.*, liii., 782) have shown that while potassium nitrate melts at 339° and sodium nitrate at 316°, a mixture of these two salts

in molecular proportion melts at 231°. Consequently, this mixture was next tried with the rare earth nitrates, the details of the method being as follows:—

The oxalates of the rare earths, after being freed from iron, as above described, are placed in porcelain evaporating dishes, the oxalates being covered with funnels of such size that when inverted they fit inside the edge of the evaporating dish. Concentrated nitric acid is now poured over the oxalates. Action begins at once in the cold, but it can be greatly hastened by warming on a water-bath. After the nitrogen oxides cease to come off, and the liquid has become clear, the solution, which should be so concentrated as to be syrupy in consistency, is poured, while still hot, into large porcelain crucibles half-filled with the well-ground mixture of potassium and sodium nitrates. About enough of the solution to completely cover the dry nitrates is poured in, and the whole is thoroughly mixed by stirring.

For heating the crucibles a double air-bath was used. Both of the two air-baths and the two covers were lined within and without with asbestos board. Through the two covers, openings were made through which thermometers could be introduced at various points within the inner bath. The crucibles were placed in circular openings cut in a piece of asbestos board, this board resting on pipe-clay rods in the inner air-baths. The asbestos board was also pierced with many small openings to allow free circulation of air. The air-bath was heated by two Bunsen burners, the height of the flame being kept constant by means of "precision" gas-cocks.

After the crucibles have been placed in position the temperature is brought up slowly, too rapid heating being liable to cause the mass in the crucibles to swell and run over the edge. The two covers are placed in position, and a thermometer is inserted through the centre opening to such a distance that its bulb is on a level with the bottoms of the crucibles. The heat is gradually increased until the thermometer shows a temperature of 300° in the inner bath. The mixture melts at a little below 230°, and decomposition of the cerium nitrate begins almost immediately. As the temperature rises the brown fumes come off copiously, the evolution gradually lessening as the heating continues. If, after removing the covers, it is seen that the evolution of gas from the fusion has entirely ceased, then the decomposition possible at the temperature employed is complete. This usually takes from four to five hours after the temperature has risen to 300°. It was found that the cerium nitrate is not entirely decomposed even when the temperature has been kept at 350° for some time, and also that if the temperature rises above 320° the cerium oxide will contain some didymium. After the evolution of nitrogen oxides ceases, the bath is allowed to cool rapidly, since by so doing the solid mass can usually be removed by inverting the crucible and tapping the edge gently. If it cannot be removed in this way, it can usually be loosened by throwing a jet of hot water around the upper edge. The removal of the mass in a solid block is of advantage, since the condition of the decomposition may be judged by the colour of the oxide which has collected at the bottom. If it is bright yellow or nearly white the ceria is probably pure, but if brownish in colour then some of the didymium nitrate also has been decomposed.

The solid mass is now treated with hot water, which dissolves all but the oxides. These are allowed to settle, and the supernatant liquid is decanted off through a filter. More hot water, containing from 4 to 5 per cent of nitric acid, is poured over the oxides, and the liquid is brought to boiling and poured, while hot, through the filter. This is repeated six times, and finally the oxides are washed with hot water alone, the washing being continued until the wash-water gives no precipitate with ammonia.

The oxides are dissolved by heating them with concentrated sulphuric acid until fumes of sulphur trioxide begin to escape, allowing the mass to cool, and then treating it with a large amount of water. More rapid solution can, however, be effected by throwing a jet of water upon the hot sulphates and stirring the mass constantly. There is some tendency to spatter, but solution is obtained in much less time and with much less water than in the first procedure. A concentrated solution of cerium sulphate thus obtained showed no didymium absorption bands in a layer 30 c.m. thick.

To test the separation quantitatively, weighed amounts of pure cerium and didymium oxalates were mixed, the mixture was dissolved in nitric acid as above described, and the mass was fused with the mixed alkali nitrates. The soluble portion from the first fusion was evaporated down and again fused with the alkaline nitrates, and this solution and fusion was repeated in all four times. The temperature during each fusion was about 300°. The insoluble cerium oxide resulting from the fusions was in each case free from didymium, and of the total cerium taken more than 63 per cent was obtained completely free from didymium by the four fusions.

Another sample of the mixed nitrates was fused at about 350°. The layer of cerium oxide which collected at the bottom of the fused mass showed a brown colouration at the edges, and the insoluble residue after being carefully washed and dissolved in sulphuric acid gave the didymium bands clearly. The filtrate tested by the hydrogen peroxide method mentioned below showed some cerium still present with the didymium.

From the foregoing it will be seen that while the method is not quantitative, it is, nevertheless, quite rapid, and the yield is comparatively high. Its chief merit lies in the fact that the cerium oxide resulting from each single fusion is free from didymium, an advantage which does not seem to be possessed by the other separation methods with which the authors are acquainted.

(To be continued).

ON THE

PRODUCTION AND MEASUREMENT OF GOLD AND OTHER METALLIC SPHERES TO DETERMINE THEIR WEIGHT.*

By G. A. GOYDER, Adelaide, South Australia.

(Concluded from p. 193).

In order to facilitate calculations of the weight of spheres of other substances than gold the logarithms of cubes 1 to 50 are here given (Table 3), together with a few other logarithms.

1. The weight of a sphere increases as the cube of the diameter.
2. The weight of a sphere of any substance is obtained by multiplying the weight of a unit sphere of water (see 3 or 5) by the specific gravity of the substance and the cube of the diameter (Table 3; see also 7).
3. Weight of sphere of water 0·01 m.m. in diameter 0·000,000,000,523,6 of a gramme, log. $\bar{1}0{\cdot}718\ 998\ 6$.
4. Weight of sphere of gold 0·01 m.m. in diameter 0·000,000,010,210,2 of a gramme, log. $\bar{8}{\cdot}009\ 342\ 5$.
5. Weight of sphere of water 0·001 in. in diameter 0·000,000,132,404 gr., log. $\bar{7}{\cdot}121\ 901\ 2$.
6. Weight of sphere of gold 0·001 in. in diameter 0·000,002,581,87 gr., log. $\bar{6}{\cdot}411\ 934\ 4$.
7. To find the weight of a sphere of any substance, the diameter and specific gravity being known—

   Add log. of cube of diameter. (See Table 3).
   + log. of weight of unit sphere of water. (See 3 or 5 above).
   + log. of specific gravity of substance.
   } = log. of weight of substance.

* From the "Fifth Annual Report of the Council of the South Australian School of Mines and Industries, 1894."

Table II.

Assay Table, showing the Weight of a Sphere of Gold of one to twenty-five thousandths of an inch in Diameter, and the Amount of Gold in ounces, pennyweights, and grains contained in a ton of Ore, &c., from the Diameter of the Sphere of Gold obtained in an Assay of 200 grains.

Diameter of Sphere in 1000ths of an inch.	Corresponding weight of Gold Sphere in parts of a grain.	200 grains being taken for Assay, corresponding yield of Gold per ton. Ozs. dwts. grs.
1·0	0·000,002,582	0 0 0·1593
1·5	0·000,008,714	0 0 0·6831
2·0	0·000,020,65	0 0 1·1619
2·5	0·000,040,34	0 0 3·162
3·0	0·000,069,71	0 0 5·465
3·5	0·000,110,7	0 0 8·678
4·0	0·000,165,2	0 0 12·95
4·5	0·000,235,3	0 0 18·44
5·0	0·000,322,7	0 1 1
5·5	0·000,429,5	0 1 9
6·0	0·000,557,7	0 1 19
6·5	0·000,709,6	0 2 7
7·0	0·000,885,6	0 2 21
7·5	0·001,089	0 3 13
8·0	0·001,322	0 4 7
8·5	0·001,585	0 5 4
9·0	0·001,882	0 6 3
9·5	0·002,213	0 7 5
10·0	0·002,582	0 8 10
10·5	0·002,989	0 9 18
11·0	0·003,436	0 11 5
11·5	0·003,926	0 12 19
12·0	0·004,461	0 14 13
12·5	0·005,042	0 16 11
13·0	0·005,672	0 18 12
13·5	0·006,353	1 0 18
14·0	0·007,085	1 3 3
14·5	0·007,871	1 5 17
15·0	0·008,714	1 8 11
15·5	0·009,615	1 11 19
16·0	0·010,57	1 14 13
16·5	0·011,60	1 17 21
17·0	0·012,68	2 1 10
17·5	0·013,83	2 5 4
18·0	0·015,05	2 9 4
18·5	0·016,34	2 13 9
19·0	0·017,71	2 17 20
19·5	0·019,14	3 2 13
20·0	0·020,65	3 7 11
20·5	0·022,24	3 12 16
21·0	0·023,91	3 18 3
21·5	0·025,66	4 3 20
22·0	0·027,49	4 9 19
22·5	0·029,41	4 16 1
23·0	0·031,41	5 2 15
23·5	0·033,50	5 9 11
24·0	0·035,77	5 16 14
24·5	0·037,98	6 4 0
25·0	0·040,34	6 11 18

Table III.

Cubes and their Logarithms.

No.	Cube.	Log. of Cube.
1·0	1·000	0·000 000 0
1·5	3·375	0·528 273 8
2·0	8·000	0·903 090 0
2·5	15·625	1·193 820 0
3·0	27·000	1·431 363 8
3·5	42·875	1·632 204 1
4·0	64·000	1·806 180 0
4·5	91·125	1·959 637 5
5·0	125·000	2·096 910 0
5·5	166·375	2·221 088 0
6·0	216·000	2·334 453 8
6·5	274·625	2·438 740 1
7·0	343·000	2·535 294 1
7·5	421·875	2·625 183 8
8·0	512·000	2·709 270 0
8·5	614·125	2·788 256 8
9·0	729·000	2·862 727 5
9·5	857·375	2·933 170 9
10·0	1000·000	3·000 000 0
10·5	1157·625	3·063 567 8
11·0	1331·000	3·124 178 1
11·5	1520·875	3·182 093 5
12·0	1728·000	3·237 543 7
12·5	1953·125	3·290 730 0
13·0	2197·000	3·341 830 1
13·5	2460·375	3·391 001 2
14·0	2744·000	3·438 384 1
14·5	3048·625	3·484 104 0
15·0	3375·000	3·528 273 8
15·5	3723·875	3·570 995 1
16·0	4096·000	3·612 359 9
16·5	4492·125	3·652 451 8
17·0	4913·000	3·691 346 8
17·5	5359·375	3·729 114 2
18·0	5832·000	3·765 817 5
18·5	6331·625	3·801 515 2
19·0	6859·000	3·836 260 8
19·5	7414·875	3·870 103 8
20·0	8000·000	3·903 090 0
20·5	8615·125	3·935 261 5
21·0	9261·000	3·966 657 9
21·5	9938·375	3·997 315 4
22·0	10648·000	4·027 268 0
22·5	11390·625	4·056 547 5
23·0	12167·000	4·085 183 5
23·5	12977·875	4·113 203 6
24·0	13824·000	4·140 633 7
24·5	14706·125	4·167 498 2
25·0	15625·000	4·193 820 0
25·5	16581·375	4·219 620 5
26·0	17576·000	4·244 920 0
27·0	19683·000	4·294 091 3
28·0	21952·000	4·341 474 1
29·0	24389·000	4·387 194 0
30·0	27000·000	4·431 363 8
31·0	29791·000	4·474 085 1
32·0	32768·000	4·515 449 9
33·0	35937·000	4·555 541 8
34·0	39304·000	4·594 436 8
35·0	42875·000	4·632 204 1
36·0	46656·000	4·668 907 5
37·0	50653·000	4·704 605 2
38·0	54872·000	4·739 350 8
39·0	59319·000	4·773 193 8
40·0	64000·000	4·806 180 0
41·0	68921·000	4·838 351 6
42·0	74088·000	4·869 747 9
43·0	79507·000	4·900 405 4
44·0	85184·000	4·930 358 0
45·0	91125·000	4·959 637 5
46·0	97336·000	4·988 273 5
47·0	103823·000	5·016 293 57
48·0	110592·000	5·043 723 7
49·0	117649·000	5·070 588 3
50·0	125000·000	5·096 910 0

If 20 grms. of ore are taken for assay the number of grains of gold per ton is found by $x^3 \times 0{\cdot}008\,004$, in which x is the diameter of the sphere of gold obtained in hundredths of a millimetre.

Log. (of 0·008 004 =) $\bar{3}{\cdot}903\,307\,1$ + log. of cube = log. of grains per ton.

If 200 grs. of ore are taken for assay the number of grains of gold per ton is found by $x^3 \times 0{\cdot}2024\,186$, in

which x is the diameter of the sphere of gold in thousandths of an inch.

Log. (of 0·202,418,6 =) $\bar{1}$·306 250 5 + log. of cube = log. of grains per ton.

USE OF MERCURIC OXIDE IN ANALYSIS.*

By E. F. SMITH and PAUL HEYL.

(Concluded from p. 193).

Nickel.

THE strength of a hydrochloric solution of nickel was adjusted so as to contain, in 25 c.c., 0·1269 grm. NiO. Several portions of this solution were evaporated after the addition of mercuric oxide, and the nickel oxide was found as follows :—

I. 0·1443 grm. II. 0·1444 grm.

A repeated determination of the nickel oxide in the original solution by precipitation with alkali showed that the first result was inaccurate. In 10 c.c. of the solution there were found by precipitation with soda 0·0579 NiO, whilst the mercury method gave—

I. 0·0577 grm. II. 0·0578 grm.

These experiments with nickel were performed in platinum vessels.

The nickel sulphide, as obtained in the course of the analysis, after solution in aqua regia must be evaporated to dryness, dissolved in the smallest quantity of water, and treated exactly as above directed.

Cobalt.

The conversion of cobalt hydrochlorate into oxide by means of mercuric oxide is complete, but the procedure has little practical value, as it is extremely difficult to obtain the cobalt oxide of a sufficiently constant composition for the final weighing. The cobalt oxide which we obtained from a solution of known strength by precipitation with alkali weighed 0·1860 grm., whilst its weight on using mercuric oxide was—

I. 0·1787 grm. II. 0·1803 grm.

The metal was weighed as oxide, Co_3O_4, since we assumed that under the oxidising influence of the heated mercuric oxide its conversion into this state would be constant enough to permit weighing. The oxides obtained by the mercuric oxide method are by no means more constant in composition than those obtained by means of alkali.

As we thought that the second result (II. 0·1803) might be possibly too high, on account of an imperfect expulsion of the mercury, the residue was again heated to full redness; it thereby lost weight, and weighed 0·1761 grm. On being again ignited to slight redness for fifteen minutes, the weight increased to 0·1786 grm.

As this figure approached very closely to the result of I. (0·1787), we suspected that possibly there was formed at faint redness a definite oxide fit for weighing. Hence the oxides which had been obtained on the mercuric oxide method were removed from the crucible as completely as possible, weighed, and heated in a current of hydrogen, with the subjoined results :—

Oxide used.	Cobalt found.
I. 0·1259 grm.	I. 0·0916 grm.
II. 0·0630 ,,	II. 0·0457 ,,

Calculated for cobalt in I. :—

CoO	0·0990 grm.
Co_3O_4..	0·0928 ,,
Co_2O_3..	0·0895 ,,

Calculated for cobalt in II. :—

CoO	0·0496 grm.
Co_3O_4..	0·0465 ,,
Co_2O_3..	0·0448 ,,

An examination of these figures shows that in both cases the quantity of cobalt found lies between the quantities theoretically required for the oxides Co_3O_4 and Co_2O_3. The quantity of oxide in experiment II. was too small to permit of the deduction of a trustworthy formula. The oxide, which has a proportion of cobalt approaching most closely to that found in I. is Co_3O_4. It requires the proportion Co : O = 1 : 1·333. In this experiment the proportion appeared as 1 : 1·4. Hence on the whole we cannot depend upon the oxides of cobalt, as different conditions of temperature occasion the formation of different oxides. It may be possible to obtain at dull redness an oxide of the approximate composition of Co_3O_4, but we have here no certainty. It is therefore preferable to reduce the oxides to metal, and to weigh in this state.

Bismuth.

In separations this metal is often precipitated as an oxychloride, Its conversion by means of mercuric oxide is analytically of great importance. We first attempted to transpose the oxychloride by bringing it in contact with mercuric oxide suspended in water, evaporating, and heating the residue. But we found ourselves compelled to renounce this procedure, and we dissolved the precipitated oxychloride in a few drops of hydrochloric acid, added sufficient mercuric oxide to neutralise the acid, and an excess sufficient for the reaction. After evaporation, we proceeded as for manganese. If the residue shows here and there black spots it must be moistened with water and 1 to 2 drops of nitric acid. After evaporation and re-heating to full redness, it is weighed as bismuth ter-oxide. Porcelain crucibles must be used in this operation.

Results.

Bismuth used.	Bismuth found.
0·0945 grm.	0·0941 grm.
0·0759 ,,	0·0756 ,,

As we have used these methods repeatedly with satisfactory results, we may recommend them as effecting a considerable economy of time, and decidedly diminishing the possible introduction of impurities by the ordinary reagents.

Persoz and Berzelius used mercuric oxide as a precipitant in the separation of metals, and in Volhard's communication above mentioned the author states that he has separated ferric oxide from manganese by means of mercuric oxide. He gives, however, no results, and we have therefore taken the liberty of repeating his experiments. A solution of ferric chloride was prepared by dissolving pianoforte wire in aqua regia; 25 c.c. of this solution contained 0·1359 grm. Fe. To 25 c.c. of this solution we added 0·3 grm. manganous chloride. Mercuric oxide was added to the cold mixture, the ferric hydroxide was separated by means of the filter pump, washed with cold water, dissolved in hydrochloric acid, and again precipitated by means of mercuric oxide. This second precipitate was carefully washed, and then ignited in a weighed platinum crucible.

Volhard gives no instructions for this separation beyond the following :—"The dilute neutral solution of the chlorides was treated with mercuric oxide." In our operation we proceeded as follows :—An excess of the precipitant is added to the dilute solution of the mixed chlorides in an Erlenmeyer flask. A trace of free acid is present in the liquid. The flask is shaken, and if after the subsidence of the precipitate the supernatant liquid has a reddish or yellow colour, more mercuric oxide is added, and so, further, until the liquid is colourless. After the first iron precipitate has been dissolved on the filter in hydrochloric acid, ammonia is gradually added until

* *Zeit. für Anorganische Chemie*, vii., 82.

nearly all the free acid is neutralised, and the precipitation is repeated. Our filtrates were bound to be free from iron.

Iron used.	Iron found.	$MnCl_2$ simultaneously present.
0·1359 grm.	0·1363 grm.	0·3
—	0·1356 „	—

The total dilution in these determinations was 150 c.c. It is possible to obtain iron free from manganese and ready for ignition in forty-five minutes.

In an attempt to precipitate glucina in the manner just described, we found that under the most varied conditions it was still present in the filtrate. Hence, the attempt to separate iron from glucina was found unsuccessful.

Uranium is not completely precipitated from the solutions of its chloride in the cold even after contact for twelve hours. On evaporating the solution of the chloride to dryness, and ignition, there remained a dark green oxide (U_3O_4). As this conversion into oxide is complete, it seemed possible in that manner to effect a separation of uranium from the alkalis. Our attempts in this direction proved, however, fruitless. The non-precipitation of uranium from hydrochloric solutions led us to attempt its separation from iron in the same manner as that of iron from manganese. The results, however, were especially unsatisfactory, since as much as 85 per cent of uranium was thrown down along with the ferric oxide.

The separation of iron from nickel, effected in the same manner as with manganese, gave an approximate result. Nickel is evidently less reactive with mercuric oxide than is uranium.

Iron taken.	Iron found.	Nickel present.
0·1359	0·1372	0·1000

If a rapid analysis is required without great exactitude, this method of separation may be considered satisfactory.

The separation of iron from nickel and cobalt was effected in the same manner. The results have about the same degree of accuracy.

Volhard mentions also that aluminium can be precipitated from cold hydrochloric solutions by mercuric oxide. We made up in consequence a solution of aluminium containing glucinium chloride. On treatment with mercuric oxide, as indicated for separating iron from aluminium, we found that, on the one hand, the aluminium was not perfectly precipitated, and that, on the other, very considerable quantities of glucina were carried down along with the aluminium hydroxide.

If lanthanum hydrochlorate is treated in the cold with mercuric oxide, one-fifth of the lanthanum is precipitated as hydroxide. In hot solutions about 75 per cent of the total lanthanum is thrown down. The reaction shows approximately the same results with solutions of cerium hydrochlorate, hot or cold.

Berzelius mentions ("Lehrbuch," x., 145) that zinc may be separated from manganese by adding mercuric oxide to the hydrochloric solution of both metals. Our experience concerning hydrochloric zinc solutions and mercuric oxide is as follows:—In cold solutions the precipitation is only partial. Heat accelerates the result, and the mercuric oxide is at first distinctly white, and then black. In one case, when 0·2176 grm. of zinc oxide was present, we obtained 0·0288. This experiment was performed in the cold. In a second experiment at the temperature of 80°, we obtained, instead of 0·2176 grm. zinc oxide, 0·2047 grm. We cannot see how this process should permit of the separation of zinc and manganese, as the latter is also precipitated by mercuric oxide from the hot solutions of its salts.

An attempt to separate in this manner chrome from the alkalis gave so unsatisfactory results that the details are not given.

If we calculate the results as to the use of mercuric oxide as a precipitant, iron, chrome, and aluminium may be completely thrown down from cold solutions; whilst zinc, cobalt, nickel, uranium, glucinium, cerium, and lanthanum are only partially precipitated. In hot solutions their precipitation is more complete. As in cold solutions traces of manganese may be precipitated, it is always advisable to precipitate the iron twice in order to arrive at a complete and satisfactory separation of manganese.*

REDUCTION OF VANADIC ACID BY THE ACTION OF TARTARIC ACID, AND ITS TITRATION BY IODINE IN AN ALKALINE SOLUTION.

By P. E. BROWNING.

For some time many chemists have been engaged with the analytical chemistry of vanadium. The methods employed for this purpose are numerous and varied. They have been collected of late in a convenient manner by Valerian von Kecki in a recent pamphlet ("Die Anal. Chemie des Vanadium," Voss, Hamburg). Hence it is needless to enter upon the analytical history of this element.

In some experiments on the behaviour of the vanadium compounds I found it advantageous to determine the vanadium volumetrically, by reduction with sulphurous acid and re-oxidation with permanganate of known strength. This procedure must rank among the most accurate of volumetric methods. With some practice I succeeded in obtaining good results in this manner, but the method presents certain defects.

In the first place, it is necessary to boil for a long time, in order to expel the excess of sulphurous acid.

Secondly, much practice is required in order to recognise the final point of the reaction between vanadium tetroxide and permanganate.

To avoid these disadvantages I found it desirable to apply an iodometric method, chiefly on account of the sensitiveness of the starch reaction, with which the final point can be distinctly recognised. Such a method is that of Holverscheit. It has, however, the defect that a distillatory apparatus has to be used in which the vanadic acid is treated with concentrated hydrochloric acid and potassium bromide, and the bromine liberated is passed into a solution of potassium bromide, and the iodine separated out is titrated with sodium thiosulphite. If it were practicable to titrate directly without previous distillation, this process would have a decided advantage. To this end I used tartaric acid as a reductive agent. An excess of this acid occasions no disadvantage, and at the same time the presence of the tartaric acid prevented the precipitation of the vanadium tetroxide in an alkaline solution. The process was effected, and tested as follows:—

A solution of sodium vanadate was prepared, and its content in known volumes was determined by the sulphurous acid permanganate method. Measured portions of this solution were then treated with an excess of tartaric acid, and boiled until the liquid took a fine blue colour. The acid solution was then rendered alkaline with an excess of potassium bicarbonate, and when perfectly cold it is treated with excess of solution of iodine of known strength. After some minutes the blue colour of vanadium tetroxide disappears, and the liquid takes the colour of iodine, which can be titrated back with arsenious acid until the colour of iodide exactly disappears. A few drops of solution of iodine will then, in

* With reference to the above particulars as to the use of mercuric oxide in analysis, it may be mentioned that in the posthumous papers of Clemens Zimmerman, edited by G. Alibegoff and G. Krüss, there are included "Researches on Uranium," "On the Atomic Weights of Cobalt and Nickel," and a number of important observations on the analytical uses of mercuric oxide.

presence of starch, produce the iodine starch reaction. The results are exceedingly accurate.

The author expresses his thanks to Prof. Dr. Krüss, under whose guidance this investigation was carried out. —*Zeitschrift für Anorganische Chemie.*

ON INCREASING THE SOLUBILITY OF BASIC SLAGS.

By Prof. Dr. PAUL WAGNER.

THE author points out the importance of increasing the solubility of the phosphoric acid in basic slags. Of two samples before him, one obtained from England, under the name of Bolckow slag, is so easily decomposed that its efficacy is scarcely less than that of superphosphate. The other sample is so difficult of decomposition that if we suppose the Bolckow slag = 100 this Bohemian sample has scarcely the value of 40 The difference is referred by the author to the difference in the proportion of silica, which in the Bolckow slag is 15·80 per cent and in the Bohemian sample only 3. There appears to be a tolerably regular connection between the solubility of a slag in citric acid and its percentage of silica. He proposes therefore to increase the solubility of the slag by augmenting the proportion of silica. Some loads of sand are to be thrown into the ignited slag, and fused with it together. The solubility in the citrate solution has been thus increased from 58 to 84 per cent. Prof. Wagner puts forward the following propositions:—

1. There are ground slags the solubility of which in the citrate liquid is close upon 100 per cent, and such slags are little inferior to superphosphate in their efficacy.

2. The solubility of the ground slags of commerce in citrate liquid differs greatly according to their origin. It sinks from 100 per cent down to 90, 80, 70, and even to 40 per cent, and its manurial value decreases approximately in the same proportion.

3. One of the main conditions for a relatively high solubility in the citrate liquor is a certain percentage of silica.

4. If it is confirmed that there is no insurmountable difficulty in converting a slag poor in silica into one rich in silica, and thus considerably increasing its solubility in the citric liquor, it remains for us to prove whether, and in what proportion, the manurial efficacy of the product is increased. Experiments for this purpose have been already instituted.—*Chemiker Zeitung.*

RECENT SOPHISTICATIONS OF FOOD.

OF 37,233 samples examined in Britain, 4793 were condemned. In Holland, in six months, 398 samples, of which 148 were condemned.

In Rotterdam, of 20 samples of butter, 5 were found objectionable. The Reichert-Meissl value 18 was taken as the lowest limit. In Berne, of 13 butters 8 were falsified or bad. Two samples of so-called "import-butter" gave Reichert-Meissl values of 4·8 and 9·4, and one of them had 17·87 degrees of rancidity.

Of 7 cocoa-powders examined in Rotterdam, 2 contained extraneous starches, and in one of them ground cacao-shells were present in abundance.

Of the dried fruits examined at Rotterdam all were objectionable, either as decayed or containing zinc. Copper sulphate was found in a sample of beef. Wiley (an American expert) found all peas imported from France cupriferous, and urged their condemnation in spite of the small quantity of this metal.

In Belgium spices have often been found objectionable during the present year. Black pepper contained 30 per cent of starch. Saffron was contaminated with 50 per cent of heavy spar and honey. Another make contained vegetable fibres coloured with acid magenta.

Mustard was mixed in one case with meal, in another with turmeric, and in a third with turmeric, sand, and a fatty oil.

At Rotterdam a sample of cinnamon was mixed with ground wood. Cloves were mixed with starch.

At Berne, among 8 samples of cloves 6 were condemned, of 15 ground peppers 12, and of 19 saffrons 13.

Of 500 samples of honey 45 per cent were pronounced impure by Wiley; of 4 examined by Schaffer 2 were objected to.

Wiley detected artificial coffee beans, both new and burnt. At Berne artificial coffee beans were detected manufactured from acorns.

Wiley often detected samples of tea-leaves which had been extracted and re-dried. Lam, of Amsterdam, detected the same fraud, and of 10 samples examined by Schaffer 7 contained extracted leaves.—*Chemiker Zeitung.*

DETERMINATION AND DETECTION OF COPPER.

By M. HAUPT.

M. HAUPT recommends for the volumetric determination of copper a method which was proposed some time ago by De Haen. In applying this method the solution of a cupric salt is mixed with solution of potassium iodide. Cupric iodide is separated out, whilst there is a simultaneous liberation of iodine according to the equation—

$$2CuSO_4 + 4KI = Cu_2I_2 + 2K_2SO_4 + I_2.$$

This iodine is titrated with a decinormal solution of thiosulphate.

In determining copper in its alloys with zinc, tin, or lead, they are dissolved to the extent of 1 or 2 grms. in concentrated nitric acid, and the solution is made up with water to 100 grms. After the meta-stannic acid has subsided, the clear solution is poured off, and a weighed portion is placed in a porcelain capsule. The excess of nitric acid is neutralised with calcium carbonate, the excess of the latter is removed by means of a few drops of hydrochloric acid, and the very faintly acid liquid is mixed with potassium iodide. The iodine thus liberated is determined volumetrically. The presence of lead does not interfere.

If an alloy contains also nickel, this metal must be previously separated from the copper. To this end the author proceeds according to the method of De Wilde (CHEMICAL NEWS, lxiii., 49).

In presence of iron the determination of the copper cannot be at once undertaken. In this case the nitric acid is expelled by evaporation with an excess of sulphuric acid, the liquid is diluted with water and heated after the addition of platinum wire and metallic zinc until the supernatant liquid is colourless. The copper and the metals precipitable by zinc are thrown down, whilst the iron remains in solution in the ferrous state.

The metallic precipitate is collected and filtered through a plug of wadding free from grease. It is washed with water, dissolved in nitric acid, and the solution is used for the determination.

The reaction involved in the above method may, according to H. Thoms (*Pharm. Centrahalle*), be used for the qualitative detection of copper salts.

A dilute solution of copper sulphate (1 : 100,000) which shows no perceptible blue tint with ammonia, and gives with potassium ferrocyanide a scarcely perceptible reaction, takes a distinct yellow colour with a solution of potassium iodide. On further dilution (1 : 200,000), in which the reaction with ferrocyanide fails, solution of

potassium iodide still gives a faint yellow tint, and on the addition of starch paste shows a distinct violet colouration. This last appears even at a dilution of 1 : 500,000.

Of course, in order to obtain this reaction no other substance must be present which might also liberate iodine or prevent its separation.

One of the most usual methods for the gravimetric determination of copper is to weigh it as cuprous sulphide. Concerning the behaviour of cuprous sulphide on ignition in a current of hydrogen, there existed various discordant views until the question was finally decided by W. Hampe (*Chemiker Zeitung*, ix., 1441).

Hampe ignited a weighed portion of cuprous sulphide for a considerable time, and repeatedly, in a Rose crucible in a current of perfectly dry and pure hydrogen. It appeared that pure copper sulphide at a red heat is very slowly but completely reduced; hydrogen sulphide escapes and copper remains. The first ignitions of 0·2 grm. cuprous sulphide for thirty minutes at a moderately high temperature (ignition with a Berzelius lamp) and, as usual, after the addition of a little sulphur, gave quite constant weights. Such favourable results, however, were not obtained if the quantity of the cuprous sulphide was too large for the heat to fully penetrate. Hampe never takes more than 0·25 grm. sulphide for weighing.

If the addition of sulphur before re-weighing is omitted, about 2 m.grms. of sulphur are carried off as hydrogen sulphide in an hour at the temperature of the Berzelius lamp. This quantity is not essentially increased at a higher temperature. When about half the sulphur has escaped the decomposing action of the hydrogen is retarded, and only about 1 m.grm. is driven off in an hour's ignition. The last 2 m.grms. of sulphur require a disproportionately long time for their expulsion. Finally, there remains pure copper.

Hampe finally performed the following experiment to meet the objection that the hydrogen employed might possibly contain traces of air and that watery vapour might possibly be formed in the ignited crucible, to the influence of which the reduction of the cuprous sulphide might be attributed.

The cuprous sulphide contained in a platinum boat was introduced into a glazed porcelain tube which was heated to ignition in a combustion furnace after a current of pure dry hydrogen had previously been passed through the tube for a considerable time. Here all precautions were employed in order to obtain a perfectly dry current of hydrogen free from O before it came in contact with the sulphide. In this manner 0·25 grm. copper sulphide was completely reduced after ignition for thirty hours.

Hampe further investigated the behaviour of copper sulphide on ignition in a current of carbon dioxide. According to his communications, copper sulphide on ignition in a porcelain boat in a glass tube over the Berzelius lamp in a current of dry carbon dioxide is not converted so readily into cuprous sulphide as in a current of hydrogen in an equal time and at the same temperature. At full redness there is formed in a current of dry carbon dioxide, free from air, firstly, semi-cuprous sulphide, which then undergoes an exceedingly gradual further decomposition. The presence of sulphur dioxide was demonstrated in the escaping gases. Experiments on the determination of copper sulphide by ignition in a current of carbon dioxide in a Rose crucible did not lead to useful results, as in a short time portions of metallic copper were formed.

According to a further experiment by Hampe, we may assume that copper sulphide does not undergo any appreciable change after ignition in pure carbon monoxide.

After J. Uhl had essentially confirmed Hampe's observations on the behaviour of cuprous sulphide in a current of hydrogen (*Berichte*, xxiii., 2153), Wegscheider resumed the investigation of the same question. He placed copper sulphide in a Rose crucible and heated it for thirty minutes in the small flame of a Bunsen in a current of dry hydrogen until the bottom of the crucible became slightly red; he then allowed it to cool in a current of hydrogen. The temperature near the bottom of the crucible was between 639° and 703°. The weight found was 0·3640 grm., corresponding to 99·64 per cent of the copper taken. On further ignition for half an hour at the same temperature the sulphide underwent merely an insignificant decrease; it weighed 0·3637 grm.

It was then heated for half an hour with the full flame of a Bunsen in such a manner that the point of the flame played on the bottom of the crucible. The temperature lay between 776° and 818°. There was found on weighing 0·3634 grm., representing 99·48 per cent of the copper used. Red places were distinguishable at the bottom of the crucible.

It was then heated for half an hour with a strong Bunsen flame, so as to play over the greater part of the crucible. The weight of the cuprous sulphide fell to 0·3603 grm., corresponding to 98·63 per cent of the copper used. The temperature reached was still below the melting-point of sodium carbonate (818°). The reddening of the contents of the crucible was considerably increased, especially near the bottom of the crucible.

Ignition for half an hour with the Techu burner (which still does not fuse sodium carbonate) reduced the weight of the contents of the crucible to 0·3578 grm., equal to 97·95 of the copper.

Gentle ignition with a little sulphur in a current of hydrogen restored the weight to its original value.

Hence it appears that on heating to faint redness (at the most 650°) the values attained are sufficiently accurate. At higher temperatures the particles nearest the bottom of the crucible, and therefore most strongly heated, are converted into metallic copper. The reduction proceeds slowly, whence it is conceivable that ignition which is too strong, but also sufficiently brief, may give accurate results.

A complete reduction of larger quantities of cuprous sulphide cannot be effected with a flame which heats the bottom of the crucible to about 800°. It is practicable with small quantities.

In a further experiment cuprous sulphide was placed at the bend of a narrow U-tube of sparingly fusible glass and heated to redness in a current of pure dry hydrogen, perfectly free from air. The result of the experiment agreed with the experience obtained on ignition in a Rose crucible.

In order to avoid the careful regulation of the temperature which is required on igniting copper sulphide in a current of hydrogen, the author tried the application of a current of hydrogen sulphide. The results are always too high.

It is not practicable to use a current of coal-gas in place of hydrogen.—*Zeitschrift für Analytische Chemie.*

THE DETECTION AND APPROXIMATE ESTIMATION OF MINUTE QUANTITES OF ARSENIC IN COPPER.*

By F. A. GOOCH and H. P. MOSELEY.

Sanger's recent successful application of the Berzelius-Marsh process to the quantitative determination of arsenic in wall-papers and fabrics (*Amer. Chem. Journ.*, xiii., 431), by the comparison of test mirrors with standard mirrors carefully prepared under the conditions of the test, opens the way, naturally, to the similar estimations of minute amounts of arsenic in any substances which may be submitted to the process immediately or after suitable preparation.

The need of a rapid and at the same time trustworthy

* Contributions from the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, xlviii., October, 1894

method for the determination of traces of arsenic in copper has led us to a study of the application of Sanger's process to this special case.

It has been shown by Headden and Sadler (*American Chem. Journ.*, vii., 342) that the presence of copper in the Marsh generator is instrumental in holding back the arsenic, and our own experience is similar. It is obvious, therefore, that means must be employed for the complete removal of the copper from the arsenic before the solution of the latter is put into the reduction flask. So far as our experience goes, there is no method by which arsenic may be removed from copper easily, and without loss, aside from those methods which depend upon the volatility of arsenious chloride from solution in strong hydrochloric acid, and of such methods we give the preference on the score of rapidity in execution, accessibility of pure materials, and compactness of apparatus, to a process recently developed in this laboratory (Gooch and Phelps, *Amer. Journ. Sci.*, xlviii., p. 216) and based upon the simultaneous action of strong hydrochloric acid and potassium bromide upon the salt of arsenic.

To get the copper into condition for the application of the process of separation from arsenic, we find it sufficient to dissolve an amount not exceeding 1 grm. in nitric acid somewhat diluted with water, to add to the solution 2 or 3 c.c. of strong sulphuric acid, and to evaporate the liquid until fumes of the sulphuric acid are disengaged abundantly. A single treatment of this sort serves to remove the nitric acid so completely that no interference with the normal action of the Marsh apparatus is apparent in the subsequent operation. The residue after concentration is diluted with water to about 5 c.m.^{3} and washed into the distillation flask with an amount of the strongest hydrochloric acid (sp. gr. 1·20) equal to that of the remainder of the liquid. It is desirable that the entire volume of the liquid should not much exceed 10 c.m.^{3}. The flask, which has a capacity of 40 or 50 c.c., is inclined at an angle of about 45° and joined by means of a pure rubber stopper to a bent pipette which serves as a distillation tube. The lower end of the vertical limb of the pipette dips beneath the surface of about 5 c.m.^{3} of hydrochloric acid of half strength contained in a test-tube which is cooled and supported by water nearly filling an Erlenmeyer flask. A single grm. of potassium bromide is introduced, and the distillation (which may be completed in three or four minutes) is pushed nearly to dryness. The flask is washed out, another portion of potassium bromide is introduced, and the first distillate is introduced and re-distilled as before, excepting that the condensation is this time effected in pure water. This second operation serves merely to hold back traces of copper carried over in the first distillation, but experiment has shown that the addition of the potassium bromide in the second distillation is quite as necessary as in the first, since the bromine liberated in the process has the effect of re-oxidising the arsenic in the receiver, and so making that element non-volatile under the conditions until the reducing agent is again introduced. The free bromine in the final distillate must be re-converted to hydrobromic acid before the contents of the receiver may be introduced into the reduction flask, and we find that this effect may be most easily and unobjectionably accomplished by the addition of a little stannous chloride dissolved in hydrochloric acid of half-strength and purified from arsenic by prolonged boiling. Incidentally and simultaneously the arsenic is reduced to the arsenious form, and, though Sanger has shown that minute amounts of arsenic are completely eliminated from the solution in the reduction flask when that element is introduced in the higher form of oxidation, it is our experience that the rapidity of elimination of the arsenic is so increased by the introduction of the small amount of stannous chloride needed to bleach the bromine that the mirror appears in from five to ten minutes and is practically complete in half an hour, especially if the precaution is taken to add a little more stannous chloride, according to Schmidt's suggestion (*Zeit. fur Anorgan. Chem.*, i., 353) after the operation has been in progress about twenty minutes.

It will be remembered that Schmidt has shown that the addition of stannous chloride to the Marsh apparatus in action not only does not effect the retention of arsenic, as many other metallic salts do, but actually brings about the final evolution in the form of the hydride of that portion of the arsenic which may have been deposited during the process in elementary form upon the zinc.

We have used the Sanger apparatus in form essentially unchanged; but we find it advantageous to fill the reserve generator with zinc coated with copper by the action of a solution of copper sulphate, instead of with pure zinc, since in this way the zinc is made more sensitive to the action of the dilute sulphuric acid, while the presence of copper (which is of course out of the question in the reduction flask) can be of no disadvantage in the reserve generator, and might even serve a useful end in fixing traces of arsenic if the zinc and acid employed were not absolutely free from that element. In the formation of the mirror, too, it has proved to be an advantage to enclose the portion of the glass tube to be heated in a short thin tube of iron or nickel slightly larger than the glass tube and kept from contact with it except at the ends, which are notched and bent inward. By keeping the outer tube of metal at a low red heat it is possible to diminish the tendency, which shows more particularly when the amounts of arsenic are fairly large, toward the formation of a double mirror corresponding to the allotropic conditions of the arsenic. The exigency compels, moreover, the substitution of hydrochloric acid for the sulphuric acid usually employed in the reduction flask; but though the opinion is current that hydrochloric acid introduces difficulties in the Marsh test, we have been unable to discover any evidence of the formation of a zinc mirror in the ignition tube or to note other unfavourable action due to the use of pure hydrochloric acid. It is, of course, obvious that the hydrochloric acid used must be actually free from arsenic (as was ours), and not merely nominally so, as is often the case with the so-called arsenic-free hydrochloric acid of commerce.

The copper for our test experiments was prepared free from arsenic by electrolysing in ammoniacal solution the purest copper sulphate obtainable, and stopping the deposition before the solution had become exhausted. In this manner we were able to procure copper in which we failed to detect arsenic. This copper was dissolved in nitric acid, arsenic in the higher condition of oxidation was added, and the process of the separation of the arsenic from the copper and conversion to the mirror carried out in the manner described. The results obtained are recorded in the accompanying Table:—

Copper taken, in grms.	Arsenic taken, in m.grms.	Mirror estimated (by comparison with standard mirror), in m.grms.	Error, in m.grms.
none	none	none	none
0·7	none	none	none
0·5	0·005	0·003	0·002−
0·5	0·011	0·013	0·002+
0·35	0·020	0·015	0·005−
0·3	0·030	0·030	none
0·43	0·040	0·035	0·005−
0·44	0·050	0·040	0·010−

It is plain from these results that the method is capable of detecting sharply minute amounts of arsenic in copper and of effecting the estimation of quantities less than 0·05 m.grm. with some approximation to accuracy. There is, as Sanger has pointed out, a good deal of variation even in standard mirrors made with all possible care and precaution, and in the estimation of mirrors containing as much as 0·05 m.grm. of arsenic the uncertainty of comparison, as well as the actual variation of the mirror, is considerable.

When a sample of copper is under test which may con-

tain more than 0·05 m.grm. of arsenic, it is desirable to introduce into the reduction flask the measured solution containing the arsenic gradually and in definite portions, and to judge by the formation of the mirror in an interval of ten minutes after the introduction of portions of this test solution whether it is wiser to add the entire solution or to estimate the arsenic in the entire solution from that found in an aliquot portion.

We append the results of the analysis of several samples of commercial copper, all of which were electrolytic, and of which the last two represented, presumably, the very purest electrolytically refined copper obtainable commercially.

	Copper taken, grm.	Arsenic found, m.grm.	Percentage of arsenic.
Sample A	0·3	0·015	0·005
„ B	0·3	0·030	0·010
„ C	1·0	0·018	0·0018
	1·0	0·015	0·0015
„ D	1·0	0·005	0·0005
	1·0	0·005	0·0005

CORRESPONDENCE.

ESTIMATION OF CARBONATES AND CAUSTIC ALKALIS IN MIXTURES.

To the Editor of the Chemical News.

SIR,—The method of estimating carbonates and caustic alkalis when present together by means of a double titration with methyl orange and phenolphthalein is so convenient that the statement by P. L. Aslanoglou that the method is inaccurate should not be allowed to pass unchallenged.

Several years ago I made a series of experiments to prove the accuracy of the process, but the details I have not by me, or I should have been glad to publish them. I can only say that if Mr. Aslanoglou will repeat his experiments in the manner pointed out by Mr. Seyler, B.Sc., he will come to a very different conclusion.—I am, &c.,

J. A. WILSON.

Vale House, Newchurch-in-Rossendale,
October 22, 1894.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxix., No. 15, October 8, 1894.

Study of the Latent Heats of Evaporation of the Saturated Alcohols of the Fatty Series.—W. Louguinine.—The author has experimented on ethylic alcohol, normal propylic alcohol, isopropylic alcohol, normal butylic alcohol, isobutylic alcohol, the amylic alcohol of fermentation, and amylene hydrate.

On a Particular Case of the Action of Alkalis upon Glucose.—Fernand Gaud.—The author has utilised the method of H. Causse in his researches on the inductive capacity of glucose and on the resulting products of decomposition. By this method it is easy to follow the reaction step by step.

Production of Gaseous Formic Aldehyd intended for Disinfection.—R. Cambier and A. Brochet.—The author has prepared formic aldehyd by two methods:—1, the depolymerisation of trioxymethylene by heat; 2, direct production by the incomplete combustion of methylic alcohol. But formaldehyd, though powerfully antiseptic in the state of gas, becomes spontaneously polymerised on cooling, and is then an inert solid devoid of action upon bacteria and their spores. But if it is allowed to cool in presence of much air,—the condition which would of course occur in practice,—this process does not take place, and the formaldehyd retains its bactericide quality. Experiments made at the bacteriological laboratory of Montsouris have enabled the authors to sterilise the ordinary dust of rooms as well as cultivations of various pathogenic micro-organisms.

Production of Alumina from Clay.—Joseph Heibling.—Suppose a clay of a known strength in alumina. For each mol. of alumina we incorporate with the clay 3 mols. ammonium sulphate and an almost equal weight of neutral potassium sulphate; 1 mol. of potassium sulphate is theoretically sufficient. The whole is well worked up and made into hollow bricks. These bricks are baked at 270°—280°. The ammonium sulphate is then decomposed into acid ammonium sulphate and ammoniacal gas, which may be collected in a condenser. The acid of the acid ammonium sulphate is first thrown upon the neutral potassium sulphate, which becomes acid sulphate. The latter, at this temperature, in presence of alumina and clay, is neutralised by the alumina, forming double aluminium and potassium sulphate, *i. e.*, alum. The bricks are then extracted by methodic lixiviation. The silica may be used for cement. The alum is freed from iron by re-crystallisation, and the solution may be treated for the precipitation of the alumina by means of the ammonia which has been distilled off. To obtain the alumina in a granulated state it is spread out upon stages in a tower traversed from bottom to top by the hot moist ammonia obtained on baking the bricks. The alum is thus transformed into a mixture of ammonium and potassium sulphates and of granular alumina.

Zeitschrift für Anorgänische Chemie,
Vol. vii., Parts 1 and 2, August 4, 1894.

Critical Studies in Preparations: Preparation of Ammonium Nitrite.—S. L. Sörensen.—From 1 to 2 grms. of commercial arsenious anhydride is covered with 150 to 200 c.c. of a mixture of equal vols. of water and concentrated nittic acid (66 per cent HNO_3) in a flask holding from 2 to 3 litres. The whole is shaken up and heated on the water-bath until there is a brisk evolution of red fumes, and acid is then added at the rate of 10 to 20 drops per minute. The acid used at first is 150 c.c. nitric acid + 150 c.c. water; then, in succession, 200 c.c. HNO_3 + 100 c.c. H_2O, 250 c.c. HNO_3 + 50 c.c. H_2O, and, lastly, pure nitric acid. If the discharge of gas is interrupted in the evening, the mixture is heated in the morning to produce a brisk development of red fumes before the acid is again dropped in. With these proportions we obtain a lively regular current of gas, with a constant excess of nitric oxide and without frothing. The red vapours are passed first through a reflux condenser, and then through an empty Woulf's bottle, and lastly into a tall cylinder containing the ammonium carbonate. The bottle and the cylinder are cooled with ice-water. We ascertain that nitric oxide is still in excess by a Woulf's bottle with water inserted after the cylinder. The reaction begins at once, and the saline mass gradually dissolves in the water formed by the process, which is, however, not sufficient to dissolve all the ammonium nitrite at this temperature. I used for the experiment 200 grms. dry ammonium carbonate, moderately powdered. The conversion is complete in from twenty-four to thirty-six hours. To the semi-fluid mass there are added 200 c.c. of absolute alcohol; the whole, after repeated agitation, is set aside at the ordinary temperature of a dwelling-room for thirty to sixty minutes, and is then filtered. After washing with 100 c.c. of absolute alcohol, there remains a residue, chiefly ammonium carbonate, and a solu-

tion of ammonium nitrite. The latter is cooled in ice-water, and the ammonium nitrite is separated by the addition of 500 c.c. ether in portions. After standing for thirty minutes in ice water, it is decanted, the residue is covered with 50 c.c. absolute alcohol, and, after stirring, there are added from 50 to 100 c.c. of ether. After standing for a short time, it is decanted, repeating this treatment if needful, and washing the precipitate by decantation, at first with a mixture of 1 part alcohol and 3 parts of ether, and lastly with pure ether. The precipitate is as rapidly as possible rinsed on to the filter with pure ether, washed at the Sprengel pump twice or thrice with pure ether, pressing it repeatedly with a spatula, and finally freed from the last trace of ether by a brief exposure over concentrated sulphuric acid. The yield is from 50 to 60 grms. ammonium nitrite. The solid salt is indistinctly crystalline. It has a faint yellowish colour. It dissolves readily in water with absorption of heat and it deliquesces in ordinary air.

Phosphorus Pentachloride and Tungsten Trioxide.—Hugo Schiff.—The author, referring to a paper in vol. vi., p. 384, on the action of PCl_5 and WO_3, denies that the results obtained by Teclu differed from his own.

On a Humite Free from Fluorine.—Paul Jannasch and James Locke.—The authors find the composition of this mineral $Mg_5[Mg.OH]_2(SiO_4)_3$.

Experiments with the Oxides of Columbium and Tantalum.—E. F. Smith and Ph. Maas.—Columbium is probably more generally known under the name of niobium. The authors point out the volatility of its acid compound, though less characteristic than that of molybdic and vanadic acids. They obtain a bluish black product, probably the trioxide, the existence of which has not been previously established.

Journal fur Praktische Chemie.
New Series, Vol. l., Nos. 18, 19, and 20.

Communications from the Chemical Institute of the University of Kiel.—These communications comprise memoirs by Th. Curtius and C. M. Dedichen, on the Synthesis of Benzene-hydrazines by means of Hydrazin-hydrate; by Th. Curtius, on the Hydrazides and Azides of Organic Acids (Treatise I.). Treatise II., on Benzhydrazide, by G. Struve; and a paper by Th. Curtius and F. Schrader on the Metallic Double Salts of Diammonium and Diamide. These important memoirs are unfortunately too extensive for insertion.

Behaviour of Triphenylmethan Colouring-matters with Nascent Bromine.—W. Vaubel.—In former papers which appeared in this journal the author announced the following results:—(1.) The amido group effects the admission of nascent bromine in the ortho- and para-positions, as does also the monoalkylised amido-group. (2.) The alkylised effects the intro-susception of bromine only in the para- and in one ortho-position. This holds good on the supposition that nascent bromine is employed when potassium bromate is added to the hydrobromic solution of the base in question until (in about one hour) the bromine reaction becomes permanent. As expected, this reaction may be applied for the determining the constituents of a part of the triphenyl colouring-matters, as also of the leuko-bases concerned.

A Contribution to a Knowledge of the Triphenylmethan Colouring-matters.—W. Vaubel.—The author discusses the formulæ for magenta and its derivatives, proposed respectively by E. and O. Fischer, by Nietzki, and by Rosenstiehl. He considers that the first-mentioned agrees best with the reactions. The following rule may, in general, lay claim to validity:—Orange and orange-red are those colours in which the effective value of the basicity of the amido-group is expressed by $1p+10=2$ or $2p+10=3$. Green, by $2p+20=4$. Blue, by $3p+30=6$. Violet-blue, by $3p+30=6$. Violet, by $2p+40=6$. Reddish-violet, by $3p+40=7$. There is certainly here a connection between the character of the colouring-matter and the basicity of the amidic group.

The Benzene Nucleus.—W. Vaubel.—The author examines auramine and the kindred bodies, Knoll's work on the constitution of pyrazol, and on the law of the ester-formation of aromatic acids discovered by V. Meyer.

The Behaviour of some Nitrogenous Nuclei with Nascent Bromine.—W. Vaubel.—This paper does not admit of useful abstraction.

On the 2, 3-Undekadion.—M. Filetti and G. Ponzio.

Constitution of Oxybehenic Acid (Ketobehenic Acid).—M. Filetti and G. Baldracco.—The same remark applies to the two last-mentioned papers.

Products of the Action of Chlorine upon Trimethylen.—G. Gustavson.—After mono- and dichlor methylen had been fractionated out, the next constant product having a higher boiling-point was trimethylen chloride, $C_3H_6Cl_2$, boiling at 119—120°. The next compound boiled at 146—148°, of the probable composition $C_3H_5Cl_3$ Further, there was a small quantity of a substance boiling at 155—157°; it was trichlorhydrine.

On Chromium Formiate.—C. Haeussermann.—This compound separates out in the state of dark green felted needles, from a solution of chromic oxide in formic acid. It consists of chrome, 26·58; carbon, 14·30; hydrogen, 3·13; and oxygen, 55·99.

MISCELLANEOUS.

Preservation of Milk by Oxygen Gas under Pressure.—M. Villon (*Repert. de Pharmacie* and *Chemiker Zeitung*).—The milk as drawn from the cow is inclosed in tightly-fitting recipients, into which the compressed oxygen is introduced, and it is then fitted into 100 litre cans at a pressure of two atmospheres. It can then be preserved for two months without suffering any change.

Indian Tanniferous Drugs.—David Hooper (*Amer. Journ. Pharm.*) has determined the tannin in a number of plants of Indian origin, and gives the result in a table. Most of the products mentioned are too low in tannin for technical uses. The most important are:—Bridelia montana 39·4 per cent of tannin, Acacia pyasantha 33·8, Acacia decurrens 33·4, and Terminalia chabula 31·0. The last mentioned is the ordinary myrobalan. None of the other species of Terminalia here mentioned reaches 20 per cent.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Composition and Analysis of Paints.—Can any reader kindly tell me the best books on the composition and analysis of paints, the action of various components, &c.—PAINT.

MEETINGS FOR THE WEEK.

THURSDAY, Nov. 1.—Chemical, 8. "The Electromotive Force of Alloys in a Voltaic Cell," by A. P. Laurie, M.A. "The Action of Nitric Oxide on Sodium Ethylate," by G. W. Macdonald, B.Sc., and Orme Masson, M.A. "On Ethylic Butane Tetra-Carboxylate," by B. Lean, D.Sc.

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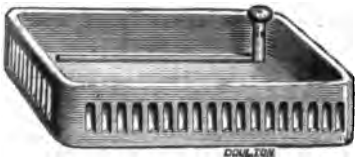

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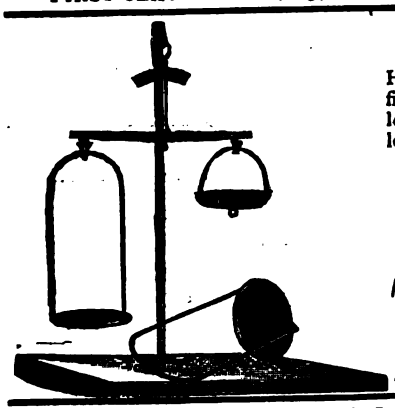

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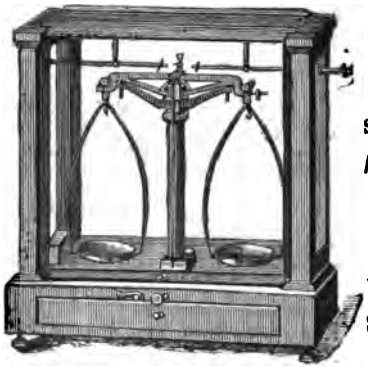

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NOTE ON

A NEW CLASS OF COMPOUNDS OF THE INACTIVE HYDROCARBONS.

By J. ALFRED WANKLYN and W. J. COOPER.

In the course of our investigation of the hydrocarbons of the Russian kerosene series, which rise by increments of 7 instead of 14 (*vide* Chemical News, lxix., p. 27), we have met with a very interesting set of weak compounds of the hydrocarbon with acetic acid. One of the greatest difficulties which has hitherto stood in the way of handling and dealing with the hydrocarbons, is the extraordinary inactivity of so many of them; hence even very weak and indefinite compounds assume an importance in this region of organic chemistry.

Our attention was first arrested by certain thermal effects which occur when glacial acetic acid is brought into contact with these liquids.

The following is the record of our first experiment in this direction:—

The temperature of 85 c.c. of the hydrocarbon B (sp. gr. 0·7586 at 17·4° C.) was very carefully measured by means of one of Casella's excellent thermometers, and recorded at 17·0° C.

Then 29 c.c. of glacial acetic acid, at a temperature of 17·5° C., was poured into the vessel containing the hydrocarbon, and the temperature of the resulting mixture was read, and found to be 13·0° C. Therefore absorption of heat to the extent of at least 4 degrees had been caused by the action of the acid upon this hydrocarbon.

The next lower hydrocarbon behaved similarly, thus:—

Hydrocarbon A*b*	175 c.c. at	19·0° C.
Acetic acid	100 ,,	18·3 ,,
	275	

were mixed together, and the temperature of the resulting 275 c.c. was found to be 14·2° C., showing a fall of temperature of at least 4 degrees.

The next lower hydrocarbon also showed similarly, thus:—

Hydrocarbon A*a*	139 c.c. at	11·7° C.
Acetic acid	56 ,,	13·0 ,,
	195	

Temperature on making the mixture 7·0° C.. which again exhibits a fall of between 4 and 5 degrees.

The next lower term of the series behaved likewise, thus:—

Hydrocarbon A*z*	111 c.c. at	16·7° C.
Acetic acid	40 ,,	16·5 ,,
	151	

Temperature on mixing 12·3° C.

In a fifth experiment a larger proportion of acetic acid was taken, thus:—

Hydrocarbon A*a* ..	50 c.c. at	10·5° C.
Acetic acid	50 ,,	12·5 ,,
	100	

Temperature on mixing, 7·3° C.

The question that we had to answer was whether the absorption was due to a physical cause, such as the becoming more fluid on making the mixture. If that were the explanation of the fall in temperature a similar effect should be observed on substituting such a hydrocarbon as benzene for the hydrocarbons which had been employed.

Benzene was accordingly taken, as follows:—

Experiment I.

Benzene..	40 c.c. at	16·5° C.
Acetic acid	10 ,,	15·6 ,,
	50	

Temperature on mixing, 15·5° C.

Experiment II.

Benzene..	50 c.c. at	9·8° C.
Acetic acid	50 ,,	9·5 ,,
	100	

Temperature on mixing, 8·5 C.

In the case of benzene there is little or no absorption of heat on admixture with acetic acid. And if "further liquefaction" were the cause of the absorption of heat in these experiments the effect should have been especially marked in the instance of benzene, inasmuch as the hydrocarbon, as well as the acid, lies open to further liquefaction, since both were near their freezing-points under the circumstances of the experiment.

Each of the four hydrocarbons obtained from Russian kerosene (which we name *kerosss*) has brought about a fall of temperature four times as great as is brought about by benzene. The cause is chemical. The large double molecule of acetic acid $(C_2H_4O_2)_2$ splits into two single molecules, $C_2H_4O_2 + C_2H_4O_2$, and absorbs heat in doing so. The single molecules of the acid enter into combination with the hydrocarbons, and in so doing evolve heat. The depression of temperature observed in the experiments is the difference between heat absorbed by the decomposition and the heat evolved by the combination.

A vapour density determination which we have made, in the case of the product of the action of the acid upon the kerose A*b*, lends some support to this view. But fractional distillation of the various products brings out, in the clearest possible manner, the fundamental differences between the character of these actions. When the benzene product is submitted to fractional distillation it behaves in a perfectly normal manner. Nothing distils until the temperature has risen to a point nearly midway between the boiling-point of the hydrocarbon and the acid. The following is the laboratory note; 99 c.c. of the mixture, consisting of equal vols. of benzene and acetic acid, were distilled:—

At 95° first drop come over.
,, 99 — 5 c.c. had distilled over.
,, 102·5—25 ,, ,,
,, 105·5—50 ,, ,,
,, 110 —75 ,, ,,

And the residue consisted chiefly of acid, yielding only 5 c.c. of hydrocarbon oil when the acid had been washed away by means of water.

Utterly different, however, were the results of fractional distillation in the five experiments upon the keroses mixed with acetic acid. In every one of these instances the kerose begins to distil much below the boiling-point of the kerose, and by the time the boiling-point of the kerose is reached most of the hydrocarbon has come over. The explanation is that the compound of kerose and acid has a somewhat lower boiling-point than that of the separate kerose, and that partial decomposition takes place during the distillation.

Details we intend to publish on a future occasion, remarking, however, that not only the keroses derived from Russian kerosene, but the marsh-gases derived from American petroleum, appear to enter into chemical combination with acetic acid. Formic acid will, we expect, act similarly, and other acids of the series we mean to

try. A most potent instrument has thus come into our hands for the separation and purification of the interesting hydrocarbons we are engaged in investigating.

Laboratory, New Malden, Surrey,
October 23, 1894.

NOTE ON THE MATTER INSOLUBLE IN WATER PRESENT IN CERTAIN ARTIFICIAL GUMS.

By J. A. WILSON.

CERTAIN artificial gums used as thickeners or stiffening agents leave a residue on treatment with water at 100° F. which would usually be stated as starch. From certain indications, I believe it is a body formed under abnormal conditions which have not been pointed out before, and I intend to study the matter further when time permits. I merely mention it now, hoping that some other chemist may have noticed it also.

THE ESTIMATION OF SULPHUR IN PYRITES.

By FRANK JOHNSON, F.C.S., &c.,
Chief Chemist at the Tharsis Mines.

IN consequence of the well-known inconvenience attending the presence of ferric salts in the solution from which sulphuric acid is to be precipitated by barium chloride, I have for the last year or two been in the habit of reducing the ferric salt to ferrous, and at the same time destroying traces of nitric acid by boiling the acid solution with a sufficiency of sodium hypophosphite.

The method, therefore, by which a large number of sulphur estimations are performed here is as follows:—

1 grm. of pyrites is weighed into a flask, 25 c.c. nitric acid added, allowed to stand for a quarter of an hour without external heat, 1½ grms. potassium chlorate dropped in, and the assay warmed for a quarter of an hour, then boiled down to dryness on a hot plate, the flask being inclined (to avoid loss by spluttering). 20 c.c. hydrochloric acid are next added, and the assay again boiled to dryness. Another 20 c.c. hydrochloric are added, and half boiled off, 50 c.c. water added, and the assay filtered from insoluble matter; the filtrate and washings made up to about 200 c.c., 1½ grms. sodium hypophosphite added, and the assay heated to boiling, when it quickly loses all yellow colour. A slight excess of barium chloride solution is then added, and the assay allowed to stand for three hours, when, if the supernatant liquor be clear, it may be filtered. The liquor is decanted on to the filter, and 1 c.c. hydrochloric acid dropped on the precipitate in the flask, followed by 100 c.c. boiling water. After five minutes this also is poured on the filter, and the washing continued as usual. The filtrate and washings amount to from 400 to 500 c.c.

Duplicate assays usually agree to less than 0·2 in about 50 per cent.

Blank assays, or checks of the reagents only, show that 0·01 to 0·02 grm. of barium sulphate are to be deducted on this account, and this is accordingly done.

I believe this method gives results about ½ per cent (*i.e.*, 0·25 in 50 per cent S) higher than would be obtained by precipitating in the presence of ferric chloride, while it is much more convenient, owing to less time and bulk of solution being required.

Tharsis Huelva, Spain,
October 19, 1894.

ON THE TRUSTWORTHINESS OF THE DETERMINATION OF PHOSPHORIC ACID AS MAGNESIUM PYROPHOSPHATE, ESPECIALLY ON THE MOLYBDENUM METHOD.*

By HUGO NEUBAUER.

THE determination of phosphoric acid as magnesium pyrophosphate, after previous separation by ammonium molybdate, is generally effected either according to the instructions of O. Abesser, W. Jani, and M. Maercker, or according to the method of B. Peitzsch, W. Rohn, and P. Wagner. In the former method the ammoniacal solution, according to the suggestion of R. Fresenius, is approximately neutralised with hydrochloric acid, then precipitated with magnesia mixture, and the determined quantity of ammonia is added.

Peitzsch, Rohn, and Wagner direct the solution of the molybdic precipitate in ammonia to be at once precipitated with magnesia mixture, added drop by drop and with constant stirring.

Neubauer applied, firstly, the latter method in the analysis of a solution of orthophosphoric acid, the quantity of which was exactly known. The phosphoric acid was separated with molybdic solution in the usual manner, the precipitate was dissolved in 100 c.c. of ammonia at 2½ per cent, and precipitated with magnesia mixture according to rule. The ignition of the precipitate was continued until, on prolonged heating over the blast, no further loss of weight was observed. The results were always too low, the errors, in case of large quantities of phosphoric acid, being very considerable.

The deficiency is due, according to the author, to the volatilisation of phosphoric acid during the ignition of the precipitate. The existence and the quantity of this loss were determined by a series of careful experiments. Higher and more correct results were obtained if the precipitate before ignition was sprinkled over with a known quantity of magnesium or calcium oxide, or if the washed precipitate is dissolved in the smallest possible quantity of hydrochloric acid and re-precipitated with ammonia and a little magnesia mixture.

The author gives the following explanation for the volatilisation of phosphoric acid:—

In presence of much ammonium salt it is possible that not all the phosphoric acid is precipitated as dimagnesium ammonium phosphate, ($MgNH_4PO_4$), but a portion of it as mono-magnesium-ammonium phosphate,—

$$Mg(NH_4)_4(PO_4)_2.$$

On ignition this compound is first split up into magnesium metaphosphate, ammonia, and water, and on the application of a stronger heat the metaphosphate is gradually changed into pyrophosphate with loss of phosphoric anhydride,—

$$2Mg(PO_3)_2 = Mg_2P_2O_7 + P_2O_5.$$

The more concentrated the solution of ammoniacal salt in which the precipitation takes place, the greater a part of the phosphoric acid is precipitated as—

$$Mg(NH_4)_4(PO_4)_2.$$

In the molybdic method, consequently, more correct results will be obtained if the ammoniacal solution of phosphoric acid is somewhat further diluted before precipitation.

The composition of the magnesic precipitate is beyond doubt further affected by the quantity of the magnesium chloride present at the precipitation. The author made therefore a series of experiments with a hydrochloric solution of pure magnesium ammonium phosphate, that is, with a solution of phosphoric acid containing phosphoric acid and magnesia in equivalent proportions.

* An Inaugural Dissertation at Rostock, 1893. (Voss: Hamberg). *Zeitschrift fur Anal. Chemie*, xxxiii., p. 362.

Each 50 c.c. of this solution, representing 0·2002 grm. phosphoric acid, was mixed with a different quantity of ammonium chloride, and there was then added to each 25 c.c. of water and 25 c.c. liquid ammonia at 10 per cent. The precipitates were filtered off, washed, and ignited with a superimposed cover, coated with magnesium oxide. Of the filtrates resulting from each pair of determinations, one was always mixed with a small proportion of solution of phosphoric salt, and the other with magnesia mixture, and the weight of the precipitate was determined.

The ammonium chloride present was in the first pair 0·3 gr., in the second 2·5, in the third 5·0, and in the fourth the solution was approximately saturated.

All the filtrates showed traces of phosphoric acid, distinct, but not ponderable. The precipitates *without* an excess of magnesium chloride have never the correct composition; they contain too much phosphoric acid, the excess being the greater the more concentrated the solution of ammoniacal salts.

If, on the contrary, the precipitate is formed with an excess of magnesium chloride, we have pure—

$$MgNH_4PO_4;$$

if at its origin, exactly so much free ammonia is present as exactly suffices for its separation. Any excess of ammonia causes the precipitate to contain too much magnesia, as a part of the phosphoric acid then seems to be precipitated as tri-magnesium phosphate.

For the detection of an excess of magnesia (or of tri-magnesium phosphate) in the precipitate, the author recommends the reaction indicated by Tollens. If the ignited phosphoric acid precipitate is suspended in water and mixed with a small quantity of a neutral solution of silver nitrate, a precipitate containing excess of magnesia turns yellow (especially if heated) in consequence of the formation of silver orthophosphate.

The experiments on obtaining pure $MgNH_4PO_4$ in an approximately neutral solution and in presence of an excess of magnesium salt, failed from the difficulty of avoiding all excess of ammonia during the precipitation. The results obtained were merely approximations.

In precipitation from a nearly neutral solution the presence of ammonium molybdate is always disturbing, as decided quantities of free molybdic acid are always carried down with magnesium-ammonium phosphate, and do not pass completely into solution on the further addition of ammonia. Such separations of molybdic acid, of course, do not occur if ammonia is present in sufficient quantity before the precipitation.

According to the author's results, the magnesian precipitate may be obtained in three different states, depending on the conditions of the solution and the manner of precipitation.

1. The precipitate is obtained in a neutral or ammoniacal solution, containing no excess of magnesian salt. In consequence the ammoniacal salts present cause the precipitate to contain less magnesia than corresponds to its normal composition. A part of the phosphoric acid is then volatilised at high temperatures and the result is too low.

2. The precipitate is formed with an excess of magnesian salt, and there is never an excess of ammonia during its formation. The precipitate has the normal composition, and the result is correct.

3. The precipitate is formed with an excess of magnesian salt, and during its formation an excess of ammonia is always present. In consequence, the precipitate contains more magnesium oxide than corresponds with its normal composition, and the result is too high.

These propositions give an explanation of the results of the various modifications of the molybdenum method. According to the procedure of Peitzsch, Rohn, and Wagner, we gradually add magnesium chloride to a solution of ammonium phosphate in excess of ammonia. On slow addition, almost the entire quantity of phosphoric acid is precipitated before an excess of magnesium chloride is present. The consequence is that the precipitate contains too little magnesia, and on ignition a corresponding quantity of phosphoric acid is volatilised. Of the very small quantity of phosphoric acid which falls down only on the presence of an excess of magnesium chloride, a small part is precipitated as trimagnesium phosphate. On the determination of very small quantities of phosphoric acid, the precipitate appears partially or entirely only in presence of an excess of magnesium chloride, and the phosphoric acid generally appears in excess.

The relations are not so simple in the process of Abesser, Jani, and Maercker, in the precipitation from an approximately neutral solution.

If magnesia mixture and ammonia are added drop by drop with constant agitation, the precipitate is generally formed only in the second or third condition. The free ammonia of the common magnesia mixture is so weak that the precipitate begins to appear only if the magnesia is in excess. The result thus becomes too high, the more so the quicker the precipitation is effected.

If the magnesia mixture contains so much free ammonia that all the phosphoric acid is thrown down at once, and without an excess of magnesia, the precipitate is obtained in the first condition and the result is too low.

It is further possible that in the formation of the precipitate the three conditions may occur in succession. This occurs when, on dropping in the magnesia mixture with agitation, the mixture contains so much free ammonia that the separation of the precipitate begins with a deficiency of magnesia, and continues until it is in excess. Here the errors may compensate each other.

All these inferences from the properties of the precipitate the author finds confirmed by direct experiments.

The results of the citrate method, therefore, of the precipitation of phosphoric acid with magnesic mixture in presence of much ammonium citrate, agree with the views hitherto held concerning the properties of the precipitate. The precipitate separated in the ordinary manner is generally formed in the third condition, since the ammonium citrate delays its separation. Hence only a small portion of phosphoric acid is found volatile on ignition. But if to an ammoniacal solution of phosphoric acid containing ammonium citrate (but containing no bases which might form with the phosphoric acid sparingly soluble compounds) we add purposely magnesia mixture, so slowly that the main quantity of the precipitate is formed with a deficiency of magnesia, the greatest part falls in the condition 1; then, on strong ignition, phosphoric acid is volatilised, and the result obtained will be too low.

According to the author's experiments the molybdenum method cannot be pronounced satisfactory, either in the modification of Peitzsch, Rohn, and Wagner, nor on that of Abesser, Jani, and Maercker. It seems altogether impossible to convert the phosphoric acid in the magnesium method into perfectly pure magnesium ammonium phosphate.

Between the two modifications the author gives the preference to the procedure of Wagner, but considers it necessary to subject the result to a correction.

Neubauer has endeavoured to ascertain the analytical errors according to the above process, and has based upon the results a table of corrections. In this table the quantities of pyrophosphate found he entered as abscissæ, and the accompanying losses of magnesium pyrophosphate as ordinates of a curve in a rectangular system of co-ordinates.

The author briefly gives the following direction for the determination of phosphoric acid:—

The separation of phosphoric acid with the molybdenum solution and the washing of the yellow precipitate are effected according to the ordinary rules. We must avoid separation of free molybdic acid by too great a heat or by too prolonged standing. The washed precipitate of

ammonium-phospho-molybdate is dissolved in 100 c.c. of cold liquid ammonia (at 2½ per cent), and then mixed, drop by drop and with agitation, with about as many c.c. of the common magnesic mixture (55 grms. crystallised magnesium chloride and 70 grms. ammonium chloride in 1 litre of ammonia at 2½ per cent), as c.grms. of P_2O_5 are present. The dropping in of 10 c.c. of magnesia mixture must take at least one minute. A more rapid addition is not to be advised. After the precipitation the deposit is once briskly stirred, and filtered after standing for at least three hours. It is washed with ammonia at 2½ per cent until the reaction for chlorine disappears, dried, placed along with the filter in a well-cleaned platinum crucible which has been thoroughly ignited over the blast. After the filter has been charred in a crucible placed in a slanting position, the heat is very gradually increased, and not allowed to exceed medium redness until the precipitate appears quite white.

It is an error to attempt to expedite the combustion of the last remnant of carbonaceous matter by a strong heat. The residue is not exposed to the blast until it is perfectly white, and it is heated until the weight remains perfectly constant on ignition for half an hour. This last point must be very carefully observed. Pure magnesium pyrophosphate and a good platinum crucible do not lose one-tenth of a m.grm. on ignition for an hour. The figure from the table of corrections is added to the weight obtained, and the sum multiplied by 0·64 gives the weight of the P_2O_5 to be determined.

If it is intended to determine the phosphoric acid as magnesium pyrophosphate, the liquid (even in the absence of all bases which can form sparingly soluble phosphates) must never be directly precipitated with magnesia mixture, but the molybdenum method must first be employed. This method not merely removes all the bases above referred to, but introduces into the solution a quantity of ammoniacal salts, depending exclusively on the quantity of phosphoric acid present, and thus renders possible concordant results.

QUANTITATIVE ELECTROLYTIC ANALYSIS.*

By ALEX. CLASSEN.

I.—*Measurement of the Strength of Current.*

Chemists have hitherto been accustomed to use for the measurement of a current its chemical effects, and to express the strength of the current in c.c. of detonating gas. I have elsewhere shown ("Quant. Analysis by Electrolysis," ed. 3, p. 53) that the detonating gas voltameter used for this purpose is not available for scientific measurements, and that the tension which the instrument requires may be greater than that of the experiment. I have further shown that comparative statements with the gas-voltmeter (when measuring a current without introducing the decomposition cell) are conceivable only when the sulphuric acid used is always of the same concentration, and when the platinum electrodes have the same shape and the same respective distance. Parallel experiments with two apparatus of different construction proved that the values obtained varied by 25 per cent and upwards. For measuring the strength of the current it has been hitherto customary to effect the measurement before the introduction of the cell, and not with its simultaneous insertion into the circuit. Although this manner of measurement is, according to experience, not to be entirely rejected if accurate details are given as to the form and the mutual distance of the electrodes, and the concentration of the solutions, it must still be pronounced unsuitable, as, on repeating the experiments of other analysts, we are compelled either to follow their instructions exactly, which is not always practicable,—since the electrodes may have either the shape of capsules, of crucibles, or cones,—or the experimental conditions have to be ascertained in which the methods may be applied for electrodes of different forms. The literature of recent years contains statements on the measurement of currents which seem absolutely incredible. Thus an author who has made it his task to submit the measurements of others to a critical examination, indicates the strength of current sometimes with the gas-voltmeter, without indications as to the form and the concentration of the acid; sometimes with an ammeter of very varying resistance (but without any details); and lastly, again, with the number of the elements. The current, the intensity of which was insufficient for most cases, was passed by the above-mentioned experimentalist into the cell which had either the form of a capsule, a crucible, or a cone, all having an unknown surface. The failure of the experiments was easily explained by the fact that the methods, the verification of which was in question, were impracticable or had been decorated with false results by the inventor. If the method of measuring currents hitherto in vogue may lead, from want of accurate knowledge, to such excrescences and errors, the time must have come for the final renunciation of this system, and for stating in future only the proportion of the strength of current to the polar surface of the electrode on which the deposition takes place, the density of current, ND_{100}, referred to 100 square c.m. of surface of electrode and the tension, a knowledge of which allows of the application of a method to any given form of electrode. Such instructions have been already supplied by several authors. If on measuring the current we use a detonating gas-voltmeter, or an ammeter, and insert in place of the measuring instrument the cell with electrolyte, then, as a matter of course there passes through the cell, not the current originally measured, but another, corresponding to the resistance of the electrolytes.

Herr Engelmann has made some experiments on the resistance and the polarisation of some metallic salts during the process of quantitative separation. In order that the indications obtained may admit of a comparison, platinum capsules of the same shape, and equal quantities of liquid were applied, and the position of the anode is maintained unaltered.

Prof. Classen, in concert with C. Rust, has carried out experiments on measuring the strength of the current in several cells with a single ammeter.

Prof. Classen has also, in concert with B. Thomsen, experimented on the measurement of the current in several cells with a single voltmeter.

Section IV. gives instructions on the density of current for the quantitative deposition of metals and their separation by the methods indicated by the author in concert with Drs. Neumann, Eisenberg, and Heydenreich.*

In these experiments both polished platinum capsules were used, and others rendered matt with the sand-blast, in order to decide on the suitability of the latter for the deposition of metals. I proposed such capsules for the deposition of peroxides. These matt capsules have also proved decidedly suitable for the above purpose, and are preferable for some metals, *e.g.*, mercury. For cleansing the capsules acid potassium sulphate was occasionally melted in them.

The following experiments fully confirm my remarks on the strength of current and the accuracy of the methods. The experiments show that in most cases the strength of the current may vary within wide limits, as a + or − of oxalates plays no part, so that even an inexperienced analyst must obtain results. Failures are in no case due to the methods, but to the manner of execution.

* *Berichte der Deutschen Chemischen Gesellschaft.*

* The modifications relating to the determination of antimony, cadmium, tin, and zinc, and to the separation of copper from iron, nickel, and cobalt, were performed in conjunction with Dr. Pilsty, of No. 1 Chemical University Laboratory, at Berlin.

Copper.

From a solution of the double ammonium oxalate in presence of free oxalic acid.

Employed:	Copper sulphate	1 grm.
	Ammonium oxalate	4 grms.
	Liquid	120 c.c.

Density of current in ampères:—

1·0 to 0·8
0·45 to 0·35

(ND_{100} for 100 square c.m surface).

Tension of the electrodes in volts:—

2·8 to 3·2
2·5 to 2·8 (matt platinum capsule).

Temperature:—

58° to 59°
58° to 60°

A uniform temperature for platinum capsules is most easily obtained by setting them in nickel dishes of a larger diameter.

Time:— 2 hours
2½ „

Obtained 0·2531 grm., instead of 0·2529 grm.
„ 0·2528 „ „ 0·2529 „

The deposits of copper were of a light red.

(To be continued).

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING SEPTEMBER 30TH, 1894.

By WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, October 10th, 1894.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 175 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from September 1st to September 29th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 175 samples examined, one was recorded as "clear but dull," the remainder being clear, bright, and well filtered.

The cold weather characteristics of the water supply have commenced to appear this season somewhat earlier than usual. The month of September, last year, was remarkable for an excess of bright sunshine and high temperature—conditions which favour high purity in running water by stimulating fluviatile vegetation and promoting oxidation of organic matter,—whereas the month just past has, meteorologically, contrasted unfavourably with the corresponding month in 1893 in many particulars. The temperature has been low, and the amount of sunshine has been deficient, thereby lessening the power of river and lake waters to destroy the traces of organic matter always present. In spite, however, of these unfavourable conditions, usually prevailing during the winter months, the composition of the Metropolitan waters has been very satisfactory. The oxygen required to oxidise the remnant of organic matter left is slightly less than that required in August, and the organic carbon is a shade higher, but only by an amount equal to one part in seven millions. We have recently adopted certain modifications in the estimation of organic nitrogen, suggested by Dr. Frankland, the author of the combustion process of water analysis. These seem to give more accurate results. The ratio of carbon to nitrogen has been high, showing that the organic matter in the water is mainly of vegetable origin; the results shown by the colour-meter corroborate this, and indicate the presence of peaty matters.

The rainfall during September over the Thames valley has been deficient to the extent of nearly one inch. The actual amount falling at Oxford was 1·74 inch, the average for twenty-five years being 2·66 inches.

We are, Sir,
Your obedient Servants,

WILLIAM CROOKES.
JAMES DEWAR.

CONTRIBUTIONS TO THE CHEMISTRY OF CERIUM.*

By L. M. DENNIS and W. H. MAGEE.

(Continued from p. 202).

II.—*Qualitative Tests for Cerium.*

EARLY in the work the necessity arose for testing various solutions and residues for the presence of traces of cerium, and a comparison of the different methods which have been proposed was made to ascertain which test was most distinctive and delicate.

Until 1864, when Gibbs (*Am. Journ. Sci.*, [2], xxxvii., 352) proposed his lead dioxide test for ceria, no satisfactory method for the qualitative detection of this earth was known. In 1882, Hartley (*Journ. Chem. Soc.*, xli., 202) proposed a more delicate and also a more easily applied test, using ammonium acetate and hydrogen peroxide. In 1885, Lecoq de Boisbaudran (*Comptes Rendus*, c., 605), and also Cleve (*Bull. Soc. Chim.*, [2], xliii., 57), observed that hydrogen peroxide gave to solutions of cerium salts, to which an excess of ammonium hydroxide had been added, a precipitate of the same colour as that yielded by Hartley's reagents; namely, an orange-red. Sonnenschein (*Ber. d. Chem. Ges.*, iii., 631), in 1870, had proposed the use of ceria as a test for strychnia, and Plugge (*Arch. d. Pharm.*, ccxxix., 558), in 1891, has reversed this, using strychnia as a test for ceria. Finally, Gibbs (*Am. Chem. Journ.*, xv., 546), in 1894, has proposed to substitute bismuth tetroxide for lead dioxide in his test.

Hartley appears to have been the only observer previous to Plugge to test the delicacy of the reactions proposed. He found that if a quantity of cerium salt equivalent to 1 m.grm. of the element was dissolved in 100 c.c. of water, the addition of ammonium acetate and hydrogen peroxide gave a distinctly brown or orange-red precipitate which could be filtered off, dried, ignited, and weighed. "Hence we can separate one part of cerium from 100,000 parts of liquid."

* From the *Journal of the American Chemical Society*, October, 1894. Read at the Brooklyn Meeting, August 15, 1894.

To test the delicacy of these various reactions ½ grm. of ceric oxide was dissolved, as sulphate, in a litre of water. Each c.c. of this solution would contain ½ m.grm. of ceric oxide. When 1 c.c. of this solution was diluted to 100 c.c., and 5 c.c. of the diluted solution was boiled with excess of lead dioxide and nitric acid (1 : 2), a faint yellow tint was to be observed, but 4 c.c. failed to yield a distinguishable colour; that is, 0·025 m.grm. can be detected in about 7 or 8 c.c. The bismuth tetroxide detected 0·017 m.grm. under the same conditions.

In testing Hartley's reaction, 1 c.c. containing ½ m.grm. was diluted to 103 c.c., each c.c. then containing 0·005 m.grm. of ceria. When 2 c.c. of this solution was diluted so much that with the solution of ammonium acetate and hydrogen peroxide it formed about 4 c.c., a yellow colour was visible, especially on looking downward into the test-tube held above a white surface; 0·01 m.grm of ceric oxide, or rather the cerium salt equivalent to this, can therefore be detected. Ammonium hydroxide and hydrogen peroxide gave as distinct a colour with 1 c.c.; that is, Boisbaudran's test is twice as delicate as Hartleys.

Next, Plugge's strychnia test was tried and proven to be as delicate as he claims. The strychnia solution is prepared by dissolving 1 part of strychnia in 1000 parts of sulphuric acid. The solution suspected of containing ceria, or a few c.c. of it, is rendered alkaline by sodium hydroxide, evaporated to dryness, and a drop of the strychnia solution is added. One-tenth of a m.grm. of ceria gives a distinct blue or violet colour changing to red. One-hundredth of a m.grm. gives a faint blue tinge which rapidly fades. If oxalic acid be present it must be decomposed, or the test fails. Boisbaudran's test is then the most delicate of any yet proposed.

Finally, known amounts of lanthana and didymia (mixed) and ceria in solution were mixed and Boisbaudran's test applied. A distinct colouration of the hydroxides was produced when 0·01 m.grm. of ceria was mixed with 0·1 grm. of lanthana and didymia in about 100 c.c. of solution.

To apply the test in the presence of a large excess of other rare earths, very dilute ammonium hydroxide solution should be employed, and this added drop by drop until the first permanent hydroxide remains after shaking. The hydrogen peroxide is then to be added,—only a couple of drops are needed—and the mixture well shaken. By this means the weakly basic ceria is precipitated almost alone, and the orange-red colour cannot be disguised.

III.—*Cerous Chloride.*

The ceric oxide prepared according to the directions given in the first section, was purified from any thoria present by boiling the oxalate (prepared from the sulphate) with a concentrated solution of ammonium oxalate. Any thorium oxalate dissolved was poured off, and a similar solution poured over the residual cerous oxalate. The whole was then bottled and allowed to stand for some months with occasional shaking. The mixture was then brought to boiling and the liquid again poured off, the residual oxalate being washed with a similar solution. This washed oxalate was then dissolved in nitric acid, care being taken to ensure full decomposition, and it was then almost neutralised with ammonium hydroxide. Potassium hydronitride was then added (Dennis and Kortright, *Am. Chem. Journ.*, xvi., 79) so long as it continued to throw down a precipitate. This was filtered off, leaving a solution of cerium nitrate containing only potassium and ammonium salts with possibly traces of calcium. This solution was precipitated with ammonium hydroxide and washed by decantation until a litre of the wash water left no residue on evaporation. The ceric hydroxide was then tested for calcium, potassium, &c., with the spectroscope, and proved to be free from all foreign material. This pure hydroxide has been employed to prepare salts of cerium.

As this work has been in reality only preliminary to an extended study of cerium, many of the already known salts were prepared in order to become familiar with their characteristics, but of these there is no need to speak at length.

A salt, which may probably be rightly claimed to be a new compound, was prepared while endeavouring to obtain cerium tetrachloride. This latter should be capable of existence if cerium is properly placed in the periodic system. Every other element in Group IV. of that system forms such a chloride, not even excepting lead (*Monatsh. f. Chem.*, xiv., 505). Among other attempts made, one was as follows:—

A concentrated solution of cerous chloride, obtained by dissolving ceric chloride in hydrochloric acid and evaporating, was placed in a wash-bottle surrounded by a freezing mixture (snow and salt) and dry chlorine gas run in. This was rapidly absorbed, and after a short time a white crystalline mass settled out. This was placed on a porous porcelain plate to remove the greater part of the liquid, and then the following experiments were tried with different portions.

An attempt was first made to dry it to constant weight over dry caustic potash *in vacuo*. A large, but irregular, loss of weight occurred, and the crystals evidently effloresced. On exposing it to the open air again, it gained in weight till almost as heavy as at first.

An attempt to dry it over calcium chloride gave a similar result. A portion was then dried in air, dust being excluded.

Weight of sample taken	.. .. ..	2·9824	grms.
,, ,, after	72 hours ..	2·9801	,,
,, ,, ,,	118 ,, ..	2·9790	,,
,, ,, ,,	142 ,, ..	2·9786	,,
,, ,, ,,	166 ,, ..	2·9786	,,

The chloride therefore assumes a constant weight in air.

In analysing this air-dried chloride the cerium was first precipitated from the aqueous solution of the salt by ammonium hydroxide, the precipitate was so gelatinous that it was difficult to wash it free from chlorides, and the oxide obtained by ignition of the precipitate was not of a pure yellow colour. The percentages of cerium obtained in two analyses were 38·01 and 38·19.

In two other samples the cerium was thrown down by ammonium hydroxide, and hydrogen peroxide was added. The orange-coloured hydroxide thus formed was not as gelatinous as that formed with ammonia alone, and was much more easily washed; but on ignition of the precipitate the resulting ceric oxide was of a pale pink colour. This colour may have been due to the presence of a small amount of a higher oxide, for the results—38·01 and 37·93 per cent cerium—while not agreeing as well as could be wished, were too high (see analysis below). The chlorine was determined by precipitation as silver chloride, and the water by the method suggested by Kraut (*Zeit. Anal. Chemie*, ii., 242):—

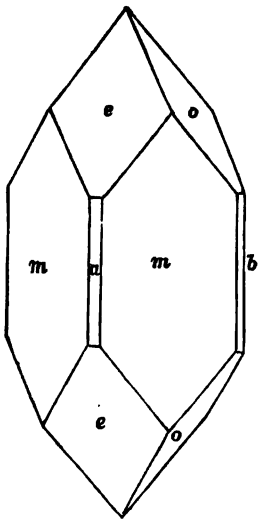
	Calculated for $CeCl_3.7H_2O$.	Found.
Ce	37·63	37·97
Cl	28·54	28·58
H_2O	33·83	33·88

The above analysis showed that the compound formed by passing chlorine into a cold saturated solution of cerous chloride was merely a finely crystalline form of cerous chloride, and not a ceric chloride. Inasmuch, then, as the formation of the compound was probably due, not to the oxidising action of the chlorine, but to its dehydrating power, it seemed reasonable to expect that dry hydrochloric acid gas would accomplish the same result. The hydrochloric acid gas was made by the action of concentrated sulphuric acid upon solid ammonium chloride; the apparatus of Norblad being used for this purpose. Upon passing the gas into a cold concentrated solution of cerous chloride, the same white finely-crystalline com-

pound separated as with the chlorine. This was dried in the air to constant weight, and then analysed. In determining the cerium, the orange-coloured hydroxide was precipitated by ammonium hydroxide and hydrogen peroxide, but, before filtering, the solution was heated just to boiling. The suspended hydroxide changed to a bright yellow colour, but it did not become gelatinous, and was easily washed. On ignition it yielded a ceric oxide of the usual pale yellow colour.

	Calculated for $CeCl_3.7H_2O$.	Found.	
Ce	37·63	37·70	37·71
Cl	28·54	28·41	28·45
H_2O..	33·83	by diff. 33·89	33·84

The crystalline form of the chloride was kindly determined by Mr. A. S. Eakle, of the Geological Department



of the University, who states that, "the cerous chloride is orthorhombic in crystallisation, and of the form shown in the figure.

The axial ratio $\breve{a} : \bar{b} : c = 0{\cdot}80834 : 1 : 1{\cdot}44187$.

$a = \infty P \bar{\infty}$ (100)
$b = \infty P \breve{\infty}$ (010)
$e = P \bar{\infty}$ (101)
$m = \infty P$ (110)
$o = P \breve{\infty}$ (011)

Faces.	Angles measured.	Angles calculated.
110 : $\bar{1}10$	77° 54′	—
110 : $\bar{1}10$	102° 12′	102° 6′
101 : 011	49° 20′	— ."

The above chloride seems to be distinct from that obtained by Jolin (*Bull. Soc. Chim.*, [2], xxi., 153) and by Lange (*Journ. Prakt. Chem.*, lxxxii., 129) for which the formula $2CeCl_3.15H_2O$ is generally given (Gmelin, Kraut, Dammer, and others). That chloride may be made by dissolving ceric hydroxide in hydrochloric acid and evaporating on the water-bath until the solution becomes quite viscous. This solution placed in a desiccator while hot solidifies on cooling to a crystalline mass of a yellow colour. If these crystals be allowed to stand in the air, they lose their colour and a glassy coating appears to form over the surface. The differences between the results obtained by Jolin and by Lange and the variation of each of their analyses from the calculated percentages made it seem desirable to repeat the analysis of chloride prepared by Jolin's method to see if better results could not be obtained. A sample of their chloride was therefore prepared by us and analysed, but the results showed as great a variation from the theory as those already mentioned.

	Calculated for $2CeCl_3.15H_2O$.	Jolin.	Lange.	Magee.	Calculated for $CeCl_3.7H_2O$.
Ce	36·74	36·89	37·37	36·37	37·63
Cl	27·87	28·40	28·80	28·65	28·54
H_2O ..	35·39				33·83

(To be continued.)

AN EXAMINATION OF THE CHLORIDES OF ZIRCONIUM.

By F. B. VENABLE.

A ZIRCONIUM chloride of definite composition would prove a valuable compound for determining the atomic weight of the element. There are several difficulties in the way of securing such a compound.

1. The tendency to form basic chlorides.
2. The ease with which hydrochloric acid is lost through the action of heat and of dehydrating agents.
3. The presence of free hydrochloric acid.
4. The deliquescent nature of the chlorides.

It is particularly desirable that the conditions under which a definite chloride can be formed should be discovered, as zirconium seems to yield no very satisfactory compounds for the determination of the atomic weight. There have been many efforts at finding out these exact conditions.

Most text-books state that anhydrous, pure zirconium tetra-chloride can be prepared by passing dry chlorine over a mixture of charcoal and zirconia heated to a high temperature. Hermann used this sublimed zirconium chloride for the determination of the atomic weight. As Clarke says, however, little confidence can be placed in his results. Bailey (CHEMICAL NEWS, lx., 17) has recorded that, even with great care to avoid the presence of moisture, he was unable to prevent the formation of oxychlorides. He also says that in no case was it found possible to prepare the chloride free from iron and silica. The necessity for the presence of these in the materials used, or in the resulting compounds, is not very apparent. I have as yet had no opportunity of repeating his experiments.

The chlorides most commonly worked with have been those formed by the solution of the hydroxide in hydrochloric acid, followed by precipitation or crystallisation from concentrated hydrochloric acid.

Berzelius attempted to remove the excess of hydrochloric acid by heating the salt to 60° C., but was not able to obtain a definite compound. Two analyses gave—

ZrO_2..	0·332	0·485
AgCl..	0·661	1·096

The silver chloride should be about two and one-third times as much as the oxide.

Paykull dried the salt between filter-paper, and found the composition of the crystals to be $ZrOCl_2.8H_2O$, the amorphous form precipitated by hydrochloric acid being $2ZrOCl_2.13H_2O$.

Endemann has described basic or oxychlorides $Zr_3O_4Cl_4$, $ZrOClOH$, and $Zr_8O_8Cl_7(OH)_9$; Troost and Hautefeuille have described others, $Zr_2O_3Cl_2$ and Zr_2OCl_6. In fact water is so easily taken up and hydrochloric acid lost that a large number of such indefinite compounds might be prepared by slightly varying the conditions.

Nylander ("Bidrag till kännedomen om Zirkonjord. Inaug. Diss. Lund. 1864") made a series of attempts at dehydrating the chloride. He prepared the chloride by dissolving the hydroxide in hydrochloric acid and evaporating to crystallisation. The salt formed white needles easily soluble in water. They were washed with alcohol, and for analyses I. and II. were pressed between filter-paper; III. and IV. were dried over sulphuric acid. The results were as follows:—

	I.	II.	III.	IV.
Zr	27·56	25·69	30·11	31·78
Cl	21·58	21·58	23·06	23·80
Loss (H_2O)	50·86	52·78	46·83	44·12

or calculated on a dry basis:—

Zr	56·08	54·41	56·63	57·18
Cl	43·02	45·59	43·37	42·82

Again preparations were made as before. I. was dried between filter-paper; II. over sulphuric acid; III. was pressed between filter-paper and then dried over sulphuric acid; IV. was dried a long time over sulphuric acid. The analyses gave the following:—

	I.	II.	III.	IV.
Zr	28·52	34·91	37·78	35·69
Cl	21·93	26·09	25·87	21·74
Loss	49·55	39·10	36·35	42·57

or calculated on a dry basis:—

Zr	56·93	57·23	59·34	62·14
Cl	43·07	42·77	40·66	37·86

Lastly, he allowed a solution of the chloride to evaporate over sulphuric acid, washed the crystals obtained with alcohol, and pressed them between filter-paper. Analyses gave—

Zr	27·94	28·74
Cl	27·32	26·67
Loss	44·74	42·62

or calculated on a dry basis:—

	Found.		Theory.	
Zr	50·56	50·04	Zr ..	38·50
Cl	49·44	49·96	Cl_4 ..	61·50

The above results show that his preparations were indefinite oxychlorides or mixtures in varying proportions of zirconium tetrachloride and oxychloride.

Bailey repeatedly crystallised the chloride from hydrochloric acid, washed it with hydrochloric acid, and then removed the free acid.

(1.) By washing with a mixture of one part alcohol and ten parts of ether.

(2.) By gently heating the salt.

(3.) By exposing the finely divided salt at ordinary temperatures in a vacuous desiccator over potash until no hydrochloric acid appeared when air was passed over it.

The analysis was performed by dissolving the salt in water and precipitating the zirconia with ammonia, then acidulating with nitric acid and precipitating the chlorine by means of silver nitrate. By method (2) a constant and progressive diminution of chlorine was observed. Therefore no analyses were made. For the other methods he gives the results of the analyses by a statement of the relation of ZrO_2 to AgCl.

	ZrO_2 : AgCl.
Berzelius's determination	1 : 1·991
,, ,, ...	1 : 2·260
Bailey's method 1	1 : 2·206
,, ,, ,, ...	1 : 2·179
,, ,, ,, ...	1 : 2·226
,, ,, ,, ...	1 : 2·260
,, ,, 2	1 : 2·264
,, ,, ,, without washing	1 : 2·245
,, ,, ,, ...	1 : 2·309
,, ,, ,, ...	1 : 2·285
$ZrOCl_2$	1 : 2·350

These preparations are evidently mixtures also.

Hermann ("Watts's Dict.," v., 1080) states that the hydrated chloride, gotten in crystals on evaporating its aqueous solution, becomes opaque at 50° C., giving off part of the water and half of the hydrochloric acid, and leaving a basic chloride or oxychloride, $ZrCl_4.ZrO_2.18H_2O$ or $ZrOCl_2.9H_2O$. The same compound is obtained in stellate groups of white silky prisms on evaporating a solution of the chloride. These crystals when heated become white and turbid, and are converted into the anhydrous dioxychloride, $ZrCl_4.2ZrO_2$.

The conditions here are inexact, and, though Hermann may have obtained these compounds, he would doubtless find it difficult to prepare them again. While it is perfectly true that an oxychloride is formed on the evaporation of an aqueous solution of the chloride, I have been unable lo obtain the compounds he mentions. Linnemann (Chemical News, lii., 224) maintains that crystallisation from hydrochloric acid (sp. gr. 1·17) and treatment with alcohol and ether gives a fine, crystalline, snow-white, silky body, leaving 50 per cent of its weight on ignition, and therefore very nearly pure $ZrCl_4$, which should leave 52·5 per cent. He claims that this is "chiefly a neutral, not a basic compound."

My own experiments on the dehydration of this salt have extended over the past two years, as opportunity was afforded. Several series of experiments were undertaken, some along the lines attempted by others, and others by methods not tried before. In all the purified chloride obtained by repeated crystallisation from hydrochloric acid was used, the salt being still wet with the excess of the acid. There was no attempt at drying this between filter-paper. The method of preparing this salt has been fully described in a previous paper in the *Journal of Analytical and Applied Chemistry*, v., 551.

In the first experiment this chloride was washed once with water, and then put in a desiccator and dried over calcium chloride (porous desiccated). It remained in the desiccator about seven months. Even after this lapse of time it still continued to show a slight loss in weight. It yielded on analysis 48·84 per cent ZrO_2.

Another portion was placed in a jar over solid lumps of sodium hydroxide. After six weeks the loss was very slight. Careful ignition left a residue of ZrO_2 equivalent to 42·99 per cent of the original weight. There was found to be 24·44 per cent of chlorine present.

Again a portion was placed over calcium chloride, and dry air was drawn over it at the rate of about fifty litres in the twenty-four hours for six months. After the first two months it was examined weekly by the interposition of a flask containing silver nitrate to see whether hydrochloric acid was still coming off. Even after the lapse of so long a time as this it was found that the loss of hydrochloric acid continued, although it was slight. On analysis this gave ZrO_2 42·28 per cent, and Cl 24·35 per cent. Although the results in this and the experiment immediately preceding correspond fairly well, they are unsatisfactory, as they point either to a mixture of chlorides or an oxychloride of very complicated formula, and hence unsuited for the ultimate aim of the research.

Lastly, a portion was placed over concentrated sulphuric acid, and the atmosphere above it exhausted occasionally. This was kept up during two months of summer weather. The loss in the last fifteen days was about 0·02 per cent of the whole. The mass was powdery, with a slightly discoloured crust. It was all soluble in water, however, and yielded a clear colourless solution. It contained 53·30 per cent of ZrO_2. This corresponds very nearly to the formula $ZrCl_4$, and is altogether at variance with the results obtained by Nylander, and with the assertion made by Hermann that half of the hydrochloric acid was lost over sulphuric acid.

This last experiment showed the possibility of securing pure zirconium chloride, provided the excess of hydrochloric acid could be removed. It was thought that this might be done by heating in an atmosphere of hydrochloric acid. A weighed flask was so arranged that it

could be kept at a definite temperature while a stream of dry hydrogen chloride was passing through it. The temperature ranged from 100° to 110° C., and the chloride placed in the flask melted, solidifying again after the loss of the water and excess of hydrochloric acid. If the drying was done slowly enough, fine crystals of zirconium chloride were gotten which lost no further weight on being kept at 100° C. A more rapid drying left a hard white mass, which was quite hygroscopic. Heating this mass for several days did not cause any diminution in weight, provided the flask was kept full of hydrogen chloride. If the mass was heated even a short time in the absence of hydrogen chloride, then further heating caused a continuous loss of weight even in the presence of a rapid stream of hydrogen chloride. After this it was impossible to secure a constant weight.

This method of drying has been tried repeatedly on various preparations, and I regard the facts stated above as showing conclusively that a neutral zirconium chloride can be prepared and dried.

Analyses of this chloride gave the following percentages of ZrO_2:—

52·70 52·78 52·63

Experiments have already been begun with a view of utilising this body in a series of experiments looking to a revision of the atomic weight of zirconium.

In connection with this subject it may be well to mention some improvements in the method of purifying zirconium chloride. (See *Journal of Analytical and Applied Chemistry*, v., 551.)

In the first place, the separation from silica by evaporation to dryness is not complete. It is impossible to heat this chloride to the necessary temperature without such a decomposition as will render the zirconium chloride also insoluble. It is best then to make this separation as thorough as possible by heating, then to change the chloride into oxide by ignition, and to treat this several times with hydrofluoric acid until the trace of silica is all driven off. This silica is too small in amount to interfere with ordinary uses, but would have to be removed where perfect purity was demanded.

Again, where the hydroxide is dissolved in dilute hydrochloric acid, or contained so much water that the acid was greatly diluted by it, it will be found that more or less of a white insoluble powder will form on evaporating, as recommended on a water-bath, and on subsequent treatment with boiling strong hydrochloric acid. By a careful arrangement of glass-wool in a hot-water funnel, the dissolved chloride can be filtered away from this insoluble mass. It seems to be quite insoluble in hydrochloric acid, though easily dissolved by water. Analysis shows that this mass is $ZrOCl_2$, and with it was found, as an impurity, whatever silca the separation by heating failed to remove.

Lastly, my assistant, Mr. Baskerville, has shown that much time and hydrochloric acid will be saved if, in the solutions containing much iron, the zirconium hydroxide be first precipitated out by means of sulphur dioxide. This precipitate can then be dissolved in acid and purified by crystallisation, as already recommended.

Of course it need scarcely be mentioned that if silica has been removed by ignition and treatment with hydrofluoric acid, it will be necessary to fuse once more with caustic alkali and repeat the ordinary purification.—*Journal of the American Chemical Society*, xvi., No. 7.

Action of Trioxymethylene and Ferric Perchloride upon the Alcohols of the Fatty Series.—MM. Trillat and Cambier.—The authors have obtained a good general method for preparing the homologues of methylal. They cause trioxmethylene and ferric chloride to act upon the alcohols from which they seek to obtain derivatives.—*Bull. Soc. Chim. de Paris*, xi.-xii., No. 15.

PROCEEDINGS OF SOCIETIES.

UNIVERSITY COLLEGE, LONDON, CHEMICAL AND PHYSICAL SOCIETY.

Address of the President, N. Eumorfopoulos, B.Sc. *October 17th*, 1894.

The Measurement of Temperature.

A short description of the mercury thermometer was given, including the corrections to be applied for errors in graduation, change of capacity of tube, &c. The method of reading recommended was by the use of a telescope having in the eye-piece a horizontal spider-line movable by means of a graduated micrometer screw.

The normal position for reading is the horizontal. In the vertical a correction has to be made for pressure on the bulb; this can amount to 0·05 or 0·1 degree.

After a thermometer is made, the zero slowly rises and tends to a final value, this taking about three years in the case of hard glass, which is the best. On heating a thermometer, the zero is always depressed, but recovers from this in a few days in the case of hard glass.

The limits of sensitiveness of a thermometer are between 0·0001 and 0·001 degree. The existence of such limits is principally due to capillarity, the variations of the latter being probably due to a film of moisture on the inside of the tube. The readings of good thermometers, even though made of different kinds of glass, will not differ by more than 0·001 degree after appropriate corrections have been made.

A more sensitive instrument is Prof. Langley's bolometer, which depends on the variation of resistance of a thin platinum wire or ribbon. The millionth part of a degree can be detected with it.

As the definition of temperature depends on thermodynamic principles, it is necessary to compare the mercury with a gas-thermometer, and hence with the absolute scale. Chappuis has done this for certain gases. Two series of each gas were taken. The pressure at 0° C. was about 1 metre of mercury in all cases. The following are some of the results (α = mean coeff. of increase of elasticity of gas between 0° and 100°):—

	Nitrogen therm. $\alpha=0{\cdot}003675$	Hydrogen therm. $\alpha=0{\cdot}003663$	Carbonic acid therm. $\alpha=0{\cdot}003725$	
	$T_N - T_{Hg}$.	$T_H - T_{Hg}$.	$T_{CO_2} - T_{Hg}$.	
−25°	+0·216	+0·233	−17·5°	+0·082
−15	+0·109	+0·119	−10·5	+0·048
− 5	+0·030	+0·034	9·9	−0·031
+ 5	−0·025	−0·028	20	−0·040
20	−0·075	−0·085	40	−0·049
40	−0·097	−0·107	60	−0·037
60	−0·085	−0·090		
80	−0·052	−0·050		

Crafts has obtained the following results for flint-glass thermometers:—

	$T_H - T_{Hg}$.
150°	+0·35
200	+0·27
250	−0·26
300	−1·21
350	−2·48

Weinstein has obtained the following numbers by calculation from some of Regnault's determinations (Thomson and Joule's experiments lead to somewhat greater differences):—

	Excess of	
	Air therm.	CO_2 therm.
	over absolute scale.	
20	0·013	0·034
40	0·018	0·051
60	0·018	0·050
80	0·012	0·032

Hence:—

	Excess of hydrogen therm. over absolute scale.	
	From air therm.	CO_2 therm.
20	+0·003	−0·009
40	+0·007	−0·008
60	+0·013	−0·003
80	+0·014	+0·001

In other words, the hydrogen thermometer is, at such temperatures, as near to the absolute scale as can be detected at present. There is no rigorous method for testing the hydrogen thermometer at low temperatures. Only probable values can be deduced as follows:—

1. By comparison with other gases at their critical temperatures. The following are obtained from Olszewski's results:—

Approximate temp.	Nitrogen therm. $T_N - T_H$.	Oxygen therm. $T_O - T_H$.	Nitric oxide therm. $T_{NO} - T_H$.
−32°	−0·5	−0·8	
−103	−0·5	−1·0	−0·5
−118	−0·5	−1·3	−1·3
−145	−0·7	−1·8	−1·9
−152	−1·0	−2·1	
Critical temp.	−146°	−119°	−94°
Boiling-point	−194°	−181°	−154°

2. By comparison with such physical properties as can be used for the measure of temperature, *e.g.*, thermo-electric E.M.F., electrical resistance, &c.

Cailletet and Colardeau carried out a number of experiments, but only down to about −100°. Down to this temperature they all give identical results. Wroblewski took his experiments to below −200°. He compared the hydrogen thermometer with the resistance of copper and the E.M.F. of a german silver copper couple. The two former practically agreed with one another; the latter did not.

For measuring high temperatures the following methods have been adopted:—

Carnelley used a calorimetric method, in which the body heated was platinum.

Le Chatelier recommends a couple of pure platinum and platinum with 10 per cent rhodium. The E.M.F. of such a couple between 300° and 1200° is a linear function of temperature.

Joly's meldometer depends on the measurement of the expansion of a platinum ribbon when heated by a current; the instrument being standardised by two or three substances of known melting-point, such as gold, &c.

Baly and Chorley have lately constructed a thermometer in which the expanding liquid is a sodium-potassium alloy. These thermometers read up to 600°.

Callendar and Griffith's pyrometer depends on the variation of resistance of platinum with temperature. It is used both for high and low temperatures, the readings of which have to be corrected to bring them to the absolute scale.

NOTICES OF BOOKS.

An Introduction to Physical Measurements, with Appendices on Absolute Electrical Measurement, &c. By Dr. F. Kohlrausch, Professor in Ordinary at the University of Strasburg. Third Edition. Translated from the Seventh German Edition, by Thomas Hutchinson Waller, B.Sc., and Henry Richardson Procter, F.I.C., F.C.S. 8vo., pp. 476. London: J. and A. Churchill. 1894.

The author, in the Preface to the second German edition, emphasizes a truth which is generally admitted in theory and almost as generally neglected in practice. He tells us that the "mere verbal teaching of physical laws is seldom of much use, tending frequently merely to confuse the student," or, at the best, to let him develope into one of the "papier philosophen," fitted admirably for passing examinations, but impotent alike for extending and for applying truths of Science. The performance of the measurements, as here explained, will lead naturally to the execution of original work.

The work opens with an introductory chapter on errors of observation, their influence and their corrections.

Next follow instructions for determining weight and density. The precautions to be observed in weighing are fully and accurately indicated. The only question to be raised is whether, instead of a vessel placed in the balance-case and filled with caustic potash or calcium chloride, it is not preferable to use *two* vessels, the one containing concentrated sulphuric acid and the other quicklime. The instructions for verifying weights are supremely needful, if accurate work is contemplated.

The author then passes to measurements of size, with the uses of the cathetometer and ophthalmometer. Then follow measurements of atmospheric pressure, of heat, and of atmospheric humidity. The next sections concern elasticity and sound, capillarity and friction.

Under Light we have determinations with the goniometer, refractometer and spectrometer, and saccharimeter. Measurements pertaining to spectrum-analysis, to the magnifying power of telescopes and microscopes, and to photometry, are also introduced.

Colorimetry is mentioned in the Index, but on turning to the page indicated we find no description of any of the most approved instruments, or of their application in chemical and biological research.

The largest section of the work is naturally taken up with the methods of observation employed in magnetic and electrical work, and the instruments used.

In connection with this subject we have an account of the absolute system of electrical measurements.

Here a popular confusion concerning weight and mass is cleared up. We read that "The chemist, the merchant, and the doctor have nothing to do with the pressure of a body on what supports it, but solely with its mass, for to this its chemical power, its nutritive or its money value is proportional."

The set of tables appended is comprehensive and useful. Among the hydrometer tables Baumé still figures, and is made 60° = 1·7 sp. gr.

There are tables of the flame spectra of the most important light metals, and of the wave-lengths in air for the most important lines.

All students of physics who possess sufficient mathematical knowledge will find this work a most valuable aid.

Natal Stones; Sentiments and Superstitions connected with Precious Stones. By G. F. Kunz. New York: Tiffany and Co.

Precious stones have from the earliest known times been regarded with a certain amount of superstition; the ancients looked upon them not only as jewels, but gave them a quite fictitious value as amulets and charms. The Jewish superstitions regarding gems were doubtless derived from more ancient races; but the origin of the use of a special gem for each month was probably founded on the original breastplate of the High Priest, which contained twelve gems, or one for each tribe.

It is curious, in these days of advanced ideas and New Women, to find that very much of the old superstitions still linger among us; and it is rather surprising to find, as we do in this little pamphlet, what many and various attributes were (or even are) ascribed to different gems. There is, however, a great deal of fascinating interest attached to the subject, and it is worthy of note, from a chemical point of view, that, with the exception of the

diamond, all the most valuable gems, to which the prefix "oriental" is placed, are composed of crystalline alumina of different colours, such as the ruby, sapphire, emerald, topaz, &c., thus showing that carbon and aluminium, two of the commonest elements in the composition of the earth, are, in certain forms and conditions, the most valuable.

CORRESPONDENCE.

DETERMINATION AND DETECTION OF COPPER.

To the Editor of the Chemical News.

SIR,—As a friend and colleague of the late Edwin Ormond Brown, I beg you will allow me to question the accuracy of M. Haupt's communication to the *Zeitschrift fur Analytische Chemie*, which appears in your current issue (page 206):—

"M. Haupt recommends for the volumetric determination of copper a method which was proposed some time ago by De Haen. In applying this method, the solution of a cupric salt is mixed with solution of potassium iodide. Cuprous iodide is separated out, whilst there is a simultaneous liberation of iodine according to the equation—

$$2CuSO_4+4KI=Cu_2I_2+2K_2SO_4+I_2.$$

This iodine is titrated with a decinormal solution of thiosulphate."

Unless it can be shown that De Haen published before 1858, the credit of introducing the above-described process belongs to E. O. Brown, who read a paper upon it before the Chemical Society of London, and in this country the method has always been known and practised according to his instructions (see "Watts' Dictionary of Chemistry," vol. ii., p. 60, which bears date 1864). Whilst at Woolwich Arsenal (I left in 1868) Brown and I made many hundreds of analyses of copper, brass, gun metal, and of other copper alloys by this method, and we always found it to give reliable results when the precautions specially pointed out by Brown were attended to, such as the expulsion of nitrous fumes and converting the cupric salt into acetate—all important details omitted by M. Haupt in his recent account.

My statement is capable of verification by reference to published data; but, if needful, Sir Frederick Abel, head of the department at that time, or my colleagues Dr. Kellner and Mr. W. Y. Drut, would be able to speak in support of the hitherto unquestioned claim of our deceased comrade.—I am, &c.,

JOHN SPILLER.

London, October 27, 1894.

SCIENCE AND ART DEPARTMENT.

To the Editor of the Chemical News.

SIR,—I wish to draw your attention to the changes in the Syllabus of the Elementary Practical Inorganic Chemistry of the Science and Art Department. The metals Hg and Al are substituted for Bi and Mn; the acids remain the same.

There is no limitation as to mercurous or mercuric salts, so presumably both may be given; but even if we delay the introduction of the student to the analytical work for two to three months, he has even then probably but a dim notion of the nature of a salt, much less of any possible distinction between two salts of the same metal and the same acid, nor can he be expected to understand the theories of variable and constant valency.

Instead, then, of having a ground-work of knowledge to guide and help him in this work, which alone can give it much training value, the whole is reduced to a mere rule-of-thumb uncomprehended testing process.

There may be wisdom in the change, political wisdom, following, and improving upon, the example of those who resist any mending where they desire ending. It may be the change was made by one hopeless of initiating a better state of things in this examination otherwise than by making it ludicrous as well as useless, thinking that the last straw might break the camel's back, or an additional absurdity bring about a radical reform.

Meanwhile what is to be done? I would gladly join in any movement to obtain, if not an immediate and thorough change, at least an alteration in the existing Syllabus.—I am, &c.,

H. E. BROTHERS.

Chemical Laboratory, Victoria Institute, Tunstall, Staffordshire, October 27, 1894.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxix., No. 16, October 15, 1894.

Application of Trouton's Law to the Saturated Alcohols of the Fatty Series.—W. Louguinine.—The author's experiments confirm the empirical law of Trouton. He found for two of the alcohols studied numbers very close upon 26·30 for ethylic alcohol, and 26·20 for amylic alcohol.

Action of Sulphur Chloride upon the Cupric Derivatives of Acetylacetone and Benzoyl Acetone.—Victor Vaillant.—On causing sulphur chloride S_2Cl_2 to act upon the cupric derivative of benzoylacetone, we obtain dithiobenzylacetone mixed with a mahogany-brown oil, very viscid, which is not easily separated. This substance crystallises in the orthorhombic form, and the crystals present the same facettes as those of dithioacetylacetone. We also obtain a cupric derivative, and a red colouration with ferric chloride.

Determination of Glucose by Cupro-alkaline Liquids.—Fernand Gaud.—The author has experimented with solutions containing 34·65 grms. copper sulphate dissolved in a sufficiency of water and made up to 1000 c.c. with ordinary ammonia. The error found was very slight compared with that occasioned by Fehling's liquid.

Pine Tar.—Adolphe Renard.—The author has discovered a new hydrocarbon boiling about 250°—280°. When rectified it is a colourless liquid boiling at 254°—257°. Its sp. gr. at 0° = 0·9419. It has no action on polarised light. Its analysis and its vapour density give figures corresponding to the formula $C_{14}H_{22}$.

Action of the Sands and the Waters of the Sahara upon Cements and Hydraulic Mortars.—Jules Perret.—The presence of a large proportion of calcium sulphate in the sands and the waters of the Sahara is most injurious to the quality and preservation of mortars prepared from cement in this region. Great care should be taken in the choice of these ingredients, especially of the sand.

Bulletin de la Société Chimique de Paris. Series 3, Vols. xi.-xii., No. 15.

The President, Scheurer-Kestner, exhibited a hymenopterous insect having an ovipositor strong enough to pierce lead. It was found making its way through a

sheet of lead spread out on deal planks. The author had repeatedly observed the same fact during the construction of lead chambers.

At the Session of July 4, 1894, two "sealed papers" were deposited, dated respectively June 24 and June 29.

Combustion-heat of the principal Gaseous Hydrocarbons.—MM. Berthelot and Matignon.—The authors have experimented with their calorimetric bomb containing compressed oxygen, upon hydrogen, carbon monoxide, formene, ethylene, ethane, propane, allylene, propylene, and trimethylene. According to the authors' figures, the difference of the combustion-heats of homologous carbides is approximately constant, and close upon 157 calories.

Method for Studying the Gaseous Interchange between Living Organisms and the Surrounding Atmosphere.—M. Berthelot.—When operating, *e.g.*, on the leaves of plants, he arranges them in a flat-bottomed capsule in a very thin layer under a large glass bell, containing about 4½ litres, and adjusted on a plate of unpolished glass. After some days, he passes slowly, by aspiration, bubble by bubble, a current of pure dry air, introduced about the centre of the bell, and continued for four to five hours. The gas escaping issues at the upper part. The volume of air is determined by the volume of water escaping from the aspirator. This volume will be, *e.g.*, equal to the volume of air contained in the bell. The carbonic acid in the air extracted from the bell is determined gravimetrically by means of two tubes containing potassa, solid and in solution. This operation is repeated once or twice weekly, until the regular decrease of carbonic acid contained in the same volume of air indicates that there is no further production of this gas, which is suspended by the desiccation which arrests all vital action. The proportion of carbonic acid contained in the bell at each exhaustion is easily calculated from the quantity extracted. We may thus study in a continuous manner the production of carbonic acid by the plant.

Sublimation of Red and Yellow Mercuric Iodides.—M. Berthelot.—This compound exists in the gaseous state only in a single form, the yellow state.

MISCELLANEOUS.

A Dangerous Water.—According to the *Medical Press*, Dr. Aston, the Medical Officer of Health for Eccleshill, has reported that the water-supply of the district contains lead to the average quantity of 1-6th grain per gallon. It is announced that in consequence iron piping is being substituted for lead in all new services in the district.

The Institute of Chemistry.—At the Examination in Practical Chemistry for admission to the membership of this Institute, held at the Laboratories at 30, Bloomsbury Square from 9th to 12th inst., seventeen candidates presented themselves, of whom the following thirteen were successful:—W. H. Archdeacon, Yorkshire College, Leeds; W. Barlow, Royal College of Science, Dublin; Miss L. E. Boole, Pharmaceutical Society's Research Laboratory; F. H. Carr, Finsbury Technical College and Pharmaceutical Society's Research Laboratory; M. E. Feilmann, B.Sc., University College, Nottingham; E. Halliwell, Yorkshire College, Leeds; E. S. Hanes, Finsbury Technical College; H. Hastings, Yorkshire College, Leeds, and student under W. Russell, F.I.C.; P. H. Jones, University College, Liverpool; W. T. Rigby, University College, Nottingham; J. S. Robertson, Glasgow and West of Scotland Technical College; E. T. Shelbourn, University College, Nottingham; and W. Thomason, University College, Liverpool. The Examiners were Professor Wyndham R. Dunstan, M.A., F.R.S., and Mr. Thomas Fairley Fairley, F.I.C.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Analysis of Paint.—In a paint containing oil, turpentine, and water (this paint is a reality), I am anxious for certain reasons to estimate the turpentine. What is the best method for this? The oil I get by drying till constant in a very thin layer on fat-free paper (as in milk analysis), and then extraction in Soxhlet.—PAINT.

MEETINGS FOR THE WEEK.

MONDAY, 5th.—Royal Institution, 5. General Monthly Meeting.
—— Society of Chemical Industry, 8. (At Burlington House). "The Composition and Constitution of certain Alloys," by the late Dr. C. R. Alder Wright, F.R.S. (to be read by Mr. Watson Smith). "Note on Oxidised Linseed Oil," by Mr. W. F. Reid.

FRIDAY, 9th.—Physical 5. "The Photographic Action of Stationary Light Waves." by J. Larmor. "On Vapour Pressure," by Prof. S. Young. "On the Luminescence of Glass," by John Burke.

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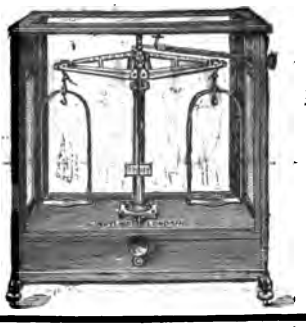

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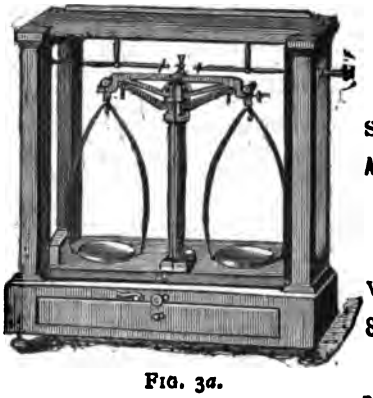

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THE FREE OXYGEN OF THE ATMOSPHERE.

By Dr. T. L. PHIPSON,
Graduate of the Faculties of Science and Medicine of the University of Brussels;
Fellow of the Chemical Societies of London, Paris, Antwerp, &c.

The ancients looked upon the air as an element, and I have shown (Chemical News, 1893 and 1894; *Comptes Rendus, id.*) that in the earliest ages of the globe it was really so, for the atmosphere must then have consisted of nitrogen only, and the free oxygen which now forms part of the air we breathe is entirely the product of plant-life extending over countless ages.

Since the days when Priestley showed that air made impure by a burning candle could be rendered pure again by the vegetation in it of a sprig of mint, until now, it has been admitted that green plants secrete oxygen gas; but before my publications alluded to above no one had ever shown that the vast bulk of free oxygen gas that forms part of the Earth's atmosphere was entirely due to plant-life, and that the plants of our present epoch are essentially anaërobic, as must have been those which vegetated in the primitive atmosphere of nitrogen, containing carbonic acid, and vapour.

It might be objected that the plants which first produced atmospheric oxygen must already have contained oxygen as part of their tissues. Whence did they derive that oxygen? But I have never said that plants were the creators of oxygen, only that they were *the means by which Nature has placed free oxygen gas in the atmosphere of the Earth.*

Palæontologists generally admit that the lowest forms of plant-life were the first to make their appearance, and on these would, of course, have devolved the function of preparing an atmosphere fit for the existence of animals. In experiments carried on during the past summer I have again confirmed what I have previously stated, namely, that these lower forms of plant-life are precisely those which produce oxygen most rapidly and most abundantly.

These experiments are not so simple as might be supposed at first sight. My method consists in measuring (and reducing to 30 inches barometer and 0° C.) the oxygen given off in a certain time by various unicellular Algæ and by phanerogamic plants high in the scale. These are then collected, dried at 100° C., and weighed. It was thus found that, weight for weight, the unicellular Algæ gave by far the most oxygen. In one experiment, last August, a mixture, consisting chiefly of *Protococcus* and *Chlamidomonas*, was thus compared during five days with the common weed, *Polygonum aviculare*, and found to produce, weight for weight, fifty times more oxygen than the latter! In other cases different results were obtained, but in all the excess of oxygen was largely on the side of the unicellular Algæ.

There are three important factors to be taken into account in making these observations:—The intensity of the sunlight; the temperatute of the day; and the amount of carbonic acid in the air and water in which the plants vegetate. In order to get comparable results these three factors must be the same in all cases; in other words, the experiment must be made with all the plants at the same time and in the same conditions. The most striking results were obtained with water saturated with carbonic acid, with bright sunshine, and with a temperature of 64° to 74° F.

Now between green plants, beings which are essentially anaërobic, and the more perfect animals, beings which are just as essentially aërobic, there exists a vast intermediate class which presents more or less the characteristics of both; such are the various organised ferments, fungi, and bacteria, &c., which represent the gradual transformation of the anaërobic cell into the aërobic cell under the influence of the gradual change of medium; that is, the constantly increasing amount of free oxygen in the atmosphere since the earlier geological ages.

In the common yeast fungus we have a familiar example of a cell which has undergone the influence of the change referred to — a cell which combines the plant and animal properties, and *secretes carbonic acid in the conditions in which the green unicellular Algæ secrete oxygen.* In the latter case the oxygen evolved is separated from carbonic acid and the carbon retained by the plant; in the former carbonic acid is secreted by the yeast cell just as in the higher animals, the function is far more complicated and requires a special nutriment, existence is rapid and short.

A small two-ounce bottle, containing about 5 c.grms. of green unicellular Algæ, filled with water containing carbonic acid and all the elements of a fertile soil, and exposed to sunlight every day, with only a temperature of 43° to 63° F. (and some very dark wet days, when the action was *nil* or nearly so), during the whole month of October, 1894, produced 14 c.c. of pure oxygen gas. So that *a single pound weight* of such unicellular Algæ will produce at least 420 gallons of oxygen per annum, or 42,000 *gallons in a century.*

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A NEW REACTION ILLUSTRATING THE PHENOMENON OF DISSOCIATION.

By ALEXANDER GUNN.

Dissolve about 0·2 grm. of zinc sulphate in 5 c.c. of distilled water. Add ammamonia (sp. gr. 0·880), drop by drop, until two drops in excess of the amount required to re-dissolve the precipitate. Then add 10 or 12 drops of a 10 per cent solution of sodium phosphate, and add 5 c.c. of water. This solution is perfectly bright. On applying heat the liquid becomes opaque, the turbidity increasing as the temperature rises until, when boiling, a thick curdy precipitate falls. On now immersing the test-tube in cold water the precipitate will quickly disappear, leaving the solution as bright as it was at first.

The production of the precipitate by heating can be repeated many times if care be taken to prevent loss of ammonia. If the solution be prepared with only one drop of ammonia in excess the reaction is wonderfully delicate, a momentary contact with the Bunsen-flame causing an evanescent cloud in the part of the liquid where the flame touches. The reason I recommend an excess of two drops of ammonia at first is, that the clearing of the liquid on cooling is very much quicker than with the smaller quantity. The quantity of ammonia is therefore to be noted. There seem to be only two possible explanations of the reaction — dissociation, or the loss of ammonia by heat. The latter is untenable for two reasons:—

1. The appearance of a cloud where the flame touches for an instant (before any ammonia can possibly have escaped) and its immediate disappearance on removal from the source of heat.
2. The complete re-solution of the heavy precipitate on cooling the solution.

Dissociation as the cause is well supported by the following experiments:—

If air be drawn through the ammoniacal solution until all the free ammonia is driven off, a white granular precipitate is thrown down, which, when collected and washed, gives off ammonia on treatment with fixed alkali.

When the clear original solution is boiled a thick curdy precipitate falls, which when collected and washed gives off no ammonia on treatment with potash or lime.

On cooling the supernatant fluid containing this precipitate, the whole becomes perfectly bright, and has no doubt reverted to its original state. This was proved by drawing air through the cooled solution, and again testing the precipitated zinc salt for ammonia, of the presence of which abundant evidence was obtained.

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ON A SIMPLE METHOD OF WORKING UP MOLYBDENUM RESIDUES, AND ON SOME EXPERIENCES IN THE DETERMINATION OF PHOSPHORIC ACID BY THE MOLYBDENUM METHOD.

By H. BORNTRÄGER.

For the analyst it is admittedly an unpleasant task to recover the valuable molybdenum residues from the determination of phosphoric acid. I have therefore sought for a simple method, which I now communicate.

The method is founded upon the fact that molybdic acid is readily soluble in ammonia, alkaline lyes, and strong nitric acid, but is almost insoluble in water, in weak nitric acid, and, of course, in other acids.

I proceed, therefore, as follows:—

As in the filtrates there is more acid than base, I pour one-fourth ammonia into a large, wide-necked flask, and add, then, at once both the acid and the ammoniacal filtrates. There appears, either at once, or in a short time—preferably at once—a separation of molybdic acid in fine crystallinic needles. It is absolutely pure. When the flask is nearly full, I render it almost neutral, allow it to settle, filter it through a bag or a filter, wash it once (not more often, as the molybdic acid is otherwise redissolved), and press the precipitate slightly. I then dissolve it in a minimum of ammonia (whereby it becomes strongly heated), filter it quickly from the impurities (silica and magnesia), and reduce the filtrate with water to the specific gravity of 1·11 at 17°. Such a solution contains per litre exactly 150 grms. ammonium molybdate. I pour it into 1 litre nitric acid of sp. gr. 1·2 (made up of 400 c.c. nitric acid of sp. gr. 1·4 and 600 c.c. water), and allow it to stand for a day, so that traces of phosphoric acid may deposit as a yellow precipitate. The solution decanted off is absolutely pure. I have worked for a quarter of a year with such solutions without having ever encountered differences with the official experimental stations. This procedure is simpler than any other, and the quantities of molybdic acid which may be dissolved in the washing waters are very unimportant. I once worked up about 100 litres of washing waters for molybdic acid, and obtained only a few grms. of very impure molybdic acid.

As regards the determination of phosphoric acid by the molybdenum method my opinion is that it is not advisable—as repeatedly proposed—to obtain the ammonium-magnesium phosphate in a crystalline state, but I prefer the crystalline form.

I proceed as follows:—

I mix the ammoniacal solution of the yellow precipitate with fuming hydrochloric acid until the precipitate, as R. Fresenius recommends, does not at once dissolve. The hydrochloric acid renders the mixture very hot, which promotes precipitation. I then precipitate with magnesia mixture, and filter as soon as air bubbles rise up out of the pulverulent precipitate. As a rule this takes place in from one to two hours. I set the molybdic precipitate in hot water up to the margin of the beaker. In this manner, an analysis takes at most three-quarters of a day from dissolving a superphosphate to weighing the precipitate.

If, on the other hand, we make the solution neutral and precipitate with magnesia mixture whilst quite hot, as it has been proposed, we obtain a crystalline precipitate, not at once, but gradually. The precipitate takes a much longer time to produce, adheres very strongly to the glass, falls down imperfectly, and the dried precipitate forms very much dust when swept into the crucible with a pencil. The ammonia escapes also with more difficulty on ignition.

I recommend the incineration of the filter together with the precipitate, as I have never found any difference occasioned by this method, and time is economised.

For ignition, the new spirit-lamp of H. Barthel, of Dresden, is especially suitable. I have used it for half a year. As I formerly mentioned, a blast is quite useless for ignition. I ignite always with the simple flame, quite gently at first, and then gradually stronger. I have never been able to detect ammonia in my precipitates after ignition. Whilst the platinum crucibles are much injured in the blast, the crucible which I use here has not yet lost 1 m.grm. in weight after 350 analyses. I ascribe this solely to the Barthel burner, since spirit yields a purer flame than coal-gas, the sulphur and tarry matter in which form platinum sulphide and carbide.—*Zeit. für Anorganische Chemie.*

TOXICOLOGICAL DETECTION AND DETERMINATION OF ARSENIC.

By ERNEST BARILLOT.

The modification which we have effected in the chemical apparatus of Marsh renders it possible to follow the decomposition of the hydrogen arsenide in a tube of green (hard) glass heated to redness.

The cadaveric matter is destroyed by one of the ordinary processes, such as that of Gautier-Pouchet, or liquefied by the method of Fresenius and Babo modified by J. Ogier (gaseous HCl and ClO_3K).

The arsenic is isolated by sulphuretted hydrogen, and the sulphide is then converted into arsenious acid by oxidation with fuming nitric acid and potassium nitrate. The nitrogen acids are expelled by heating the residue to about 200° with an excess of sulphuric acid.

We thus obtain a sulphuric solution containing all the arsenic. We ascertain by means of brucine that it is free from nitric acid, and we satisfy ourselves of the absence of nitrous acid by means of metaphenylene-diamine-hydrochlorate. We then introduce the quid gradually into the Marsh apparatus, which is set n action in the ordinary manner. The gases evolved, after passing through a desiccating tube, enter a horizontal tube of green glass extending from the left to the right, and which can be heated by means of three Bunsen burners at the three successive places, A, B, and C.

The arsenic, if the apparatus is well-regulated, is deposited almost entirely on this side of B A. If the apparatus works too strongly, there is also formed a ring at B, but rarely at C.

Whenever we obtain merely a very slight ring at B, or none at all, and none at C, we may be certain that there has been no loss of arsenic. We may easily ascertain these facts by allowing the gaseous current after passing C to bubble up through an apparatus containing a solution of neutral silver sulphate.

When the apparatus has been in action for some time, and we think that all the arsenic has been expelled, we may satisfy ourselves by ceasing to heat at A, but continuing to heat at B and C. If no ring is formed, all the arsenic is passed over, but if this is not the case there are formed new rings.

The rings are cut away from the tube, according to Gautier's method, the sections of the tube are weighed

to the $\frac{1}{10}$th of a m.grm., washed in fuming nitric acid, dried, and weighed anew. We thus obtain the weight of arsenic deposited.—*Bulletin de la Société Chimique*, xi.-xii., p. 958.

VOLUMETRIC DETERMINATION OF FORMIC ACID.

By A. LIEBEN.

THE author founds his process upon the power of formic acid to reduce permanganate. Pean de Saint-Gilles formerly proposed to determine formic acid by oxidation with permanganate in an alkaline solution, and then complete the titration in an acid solution. The author states that the oxidation of formic acid by permanganate cannot be utilised for a quantitative determination in an acid solution either in the cold or on heating. The values obtained are always too low.

On the contrary it is practicable to effect a complete oxidation of formic acid in presence of sodium carbonate so as to serve for a volumetric determination. It is indifferent whether the titration is effected in cold or heat; the quantity of sodium carbonate added is also without influence upon the result.

The oxidation takes place according to the following equation:—

$$3KCHO_2+2KMnO_4=2MnO_2+2KHCO_3+H_2O.$$

The end of the titration is not so easily detected, as the red colouration produced towards the end disappears only slowly. It is hence necessary to wait for a considerable time in order to be certain of the permanent red colouration. After titration in the cold the author allows the liquid to stand covered over night in order to be convinced of the completion of the experiment by the permanence of the redness. If the titration is conducted in heat, a much shorter time is sufficient.

The accompanying analyses are satisfactory.

The author has also tried the method recommended by Scala. He finds that accurate results are obtained only if the excess of mercuric chloride added is very considerable. At least fifty times the quantity of the formic acid used, or four times the quantity theoretically required, is necessary. It is also to be recommended to heat in the water-bath not merely two hours, as Scala states, but from six to eight hours. It is indispensable after filtration to heat the filtrate for some time in the water-bath in order to be certain of the full completion of the reaction. A slight dimness may be neglected, as 1, *e.g.*, Hg_2C_2 corresponds only to 1 m.grm. formic acid.—*Monatshefte f. Chemie.*

DETERMINATION OF FLUORINE IN GASEOUS ORGANIC FLUORIDES.

M. MESLANS effects this determination by oxidation with oxygen. In presence of a sufficiency of hydrogen all the fluorine is converted into hydrofluoric acid. This can then be effected volumetrically with normal alkali or gravimetrically after conversion into insoluble calcium fluoride.

In the investigation the author uses the following apparatus:—A 500 c.c. flask of stout glass (such as is used for combustion tubes) is closed with a caoutchouc stopper having three perforations. Through one passes a glass tube fitted with a glass cock, a platinum tube being melted into the glass tube and reaching into the interior of the flask. Through the other two apertures pass two other glass tubes, in each of which there is inserted a strong platinum wire. One of these wires is connected in the interior of the flask with the platinum tube, and the other runs parallel to it. The platinum tube is surrounded with a spiral of thin platinum wire, one end of which is connected with the second platinum wire, whilst its other end touches the platinum tube. The spiral can be raised to ignition by the passage of an electric current.

In performing the experiment the flask is charged with dilute lye of known strength, the air is exhausted, and about 400 c.c. of oxygen are caused to enter. The internal pressure is to be about 10 m.m. A measured quantity of the gas in question is then slowly passed through the tube fitted with a glass cock. On issuing from the platinum tube it is at once burnt by the ignited spiral.

If the flask is grasped by the neck, brought into nearly horizontal position, and the liquid shaken so that it rinses all parts of the belly of the flask, a complete absorption of the hydrofluoric acid formed may be effected so that the glass is not attacked. As soon as the intended quantity of the gas in question has been introduced into the flask, the influx of gas is stopped, and a few c.c. of air is admitted in order to burn also the portion of the gas remaining in the tube.

It is then only necessary to determine the excess of alkali by titration in order to find the quantity of the hydrofluoric acid which has been absorbed.

If it is intended to determine the fluorine gravimetrically, we proceed in the same manner, only instead of potassa lye we introduce into the flask a sufficiency of milk of lime. After absorbing the hydrofluoric acid, the mass, containing calcium fluoride, hydroxide, and carbonate, is evaporated to dryness, so that the calcium fluoride may be more easily filtered. It is then acidified with acetic acid, and the determination of the fluorine is effected in the known manner.—*Zeitschrift f. Analytische Chemie*, xxxiii., 470.

ON INDICATORS.*

By B. REINITZER.

As an indicator for the majority of acidimetric and alkalimetric determinations I prefer to all others a solution of litmus properly prepared. In cold liquids free from carbonic acid litmus surpasses all other substances proposed for the same purpose in sensitiveness and in the definiteness of its change of colour. It is, *e.g.*, about eight times superior to methyl-orange. As compared with the latter it has also the advantage of being applicable by gas or lamp light.† Unlike phenolphthalein it does not fail in the presence of ammoniacal salts. Its high sensitiveness even to the feeblest acids is the cause why it cannot be used in presence of carbonic acid. A sharp change of colour is obtained only when working in liquids which immediately before titration have been kept in ebullition for seven to ten minutes and then strongly cooled. Even the carbonic acid on brief exposure to the air suffices to make the transition indistinct. The carbonic acid always present to a small extent in normal alkali has a disturbing effect, whence we have to arrange that after ebullition but little alkali is required to reach neutrality. A subsequent dilution of the boiled solutions with distilled water which has not been recently boiled out must be avoided, as thereby carbonic acid would be anew introduced. In standardising normal alkali with normal acid, ebullition must not be omitted. Even the use of lime-water as a standard liquid does not supersede this precaution, as I have found that lime-water dissolves a small quantity of calcium carbonate, so that even perfectly clear lime-water is not quite free from carbonic acid if during its preparation the access of carbonic acid has not been prevented by especial precautions, and if the materials used

* From the *Zeitschrift fur Angewandte Chemie*, September 15, 1894.

† Have the colours been compared by electric light?

have not been perfectly free from carbonic acid. In two determinations of carbonic acid effected by acidulation, expulsion, absorption, and weighing, I obtained in each litre of clear lime-water containing 1·1738 grm. calcium oxide respectively 0·0093 and 0·0087 grm. carbonic acid.

We may assume that the same conditions will hold good with baryta water. It must further be kept in view that in the customary directions for preparing the extract of litmus used for titration no sufficient attention is paid to its high percentage of alkaline carbonate. If according to these directions we add acid to the solution of litmus in the cold until a violet colouration appears, we have only reached an apparent neutrality. The liquid then holds carbonic acid in solution, which has an influence on the colour, as it may be easily seen if we heat the liquid to ebullition after this apparent neutralisation. The liquid turns at once to a deep and pure blue, and a relatively large quantity of acid must be added in order to really neutralise the boiling liquid. If, as it rather often happens, such solution of litmus apparently neutralised, but really containing much alkaline carbonate, is used in the cold, the result of the analysis is unavoidably affected. This is especially the case if a considerable quantity of a very dilute solution has to be titrated with decinormal solutions.

If, as it occasionally happens, we add to the liquid to be titrated after ebullition a further quantity of litmus solution, possibly on account of the colouration being indistinct, the carbonic acid present will naturally affect the sharpness of the change of colour. Hence in preparing the solution of litmus we must heat the clear extract to full ebullition, and add concentrated hydrochloric acid drop by drop until, after boiling for about seven to eight minutes, a distinct wine-red colour is obtained. It is then allowed to cool, and about an equal volume of strong alcohol is added. The salts of litmus met with in commerce are of very different quality, the inferior being scarcely fit for volumetric use.

For its preservation the most convenient arrangement is to keep the solution in a wide-mouthed bottle closed with loosely-fitting cork. The quantity needed for a titration is taken out by means of a glass tube tapering at one end and fitting firmly into a perforation of the cork. To prevent the entrance of dust, the upper end—which is closed with the finger when taking out a portion of the liquid—is kept stoppered with a small plug of wadding. This is the best method of preserving indicators.

The disregard of the great sensitiveness of the colouring matter of litmus for carbonic acid is the cause that many chemists deny its property of a sharp transition of colour, and consider it less sensitive than the indicators recently proposed. Professor Lunge has remarked on this subject: "The number of the indicators latterly proposed for acidimetry and alkalimetry is exceedingly large and is constantly increasing. Nevertheless many chemical institutions take almost no notice of them, and continue in their teachings to use quite or nearly exclusively the time-hallowed tincture of litmus. This is strange, not only because litmus, as compared with some of the new indicators, is far less convenient, but especially because it is known that the process of boiling, frequently (more correctly always) unavoidable in case of litmus, may take up alkali out of the glass, unless Bohemian beakers or porcelain beakers or porcelain dishes are used."

It is thus further pointed out that several of the new indicators are not sensitive to carbonic acid, sulphuretted hydrogen, and other very feeble acids, that they permit of titration in the cold, and are consequently preferable to litmus, besides being much more sensitive. Prof. Lunge continues: "Thomson, in accordance with many other observers, finds that methyl-orange which I proposed in 1878 is one of the most sensitive and useful indicators for alkalis, mineral acids, and in other cases."

In order to prevent a possible error it must be firstly remarked that Thomson has by no means represented methyl-orange as more sensitive than litmus. He pronounces both equal, which is certainly quite false, as I shall subsequently show litmus is far more sensitive. It is therefore, although nine years have elapsed since the above publication, used as it was previously, not only in the chemical institutions, but in the great chemical industries, and on a far more extensive scale than the more recent industries, and this with good reasons. For instance, at the Solway Ammonia-Soda Works all the titrations for superintending and guiding the working—amounting to hundreds daily—are still, as heretofore, effected with the aid of litmus.

(To be continued.)

QUANTITATIVE ELECTROLYTIC ANALYSIS.*

By ALEX. CLASSEN.

(Continued from p. 215).

Cadmium.

The separation of this metal in a compact shining condition was not found possible by any of the methods which have been proposed; but it succeeds completely and quickly by the electrolysis of a hot solution of the double oxalate, which is kept acid during the operation by the addition of a cold saturated solution of oxalic acid. In order to form the double salt we dissolve the cadmium compound in the platinum capsule in about 20 to 25 c.c. of water, with the aid of heat; add a hot solution of 10 grms. ammonium oxalate in 80 to 100 c.c. of water (previously filtered if needful), and electrolyse with a current of $ND_{100}=0·5$ to 1·5 ampère. As soon as the current begins to act we pour upon the watch-glass covering the capsule a few c.c. of oxalic acid, and keep the liquid slightly acid during the electrolysis. The metal is washed without interrupting the current. In experiments when there was used from 0·3 to 0·4 cadmium sulphate, 10 grms. ammonium oxalate, and 120 c.c. of liquid, with a density of current $=0·6—0·5$ ampère, a tension of the electrodes of 2·75 to 3·4 volt, a temperature of 72—76°, and a time of 3½ hours, the deposit obtained was 0·1472=49·07 per cent. The deposit was clear and shining.

Zinc.

This metal also is separated from a feebly acidulated solution in a perfectly metallic state, with its characteristic white colour. In this case we proceed as before; dissolve the zinc salt in a beaker, add about 4 grms. potassium oxalate, or an equal quantity of ammonium oxalate, and put the solution in a weighed platinum capsule, coated with copper. The copper coating can be obtained compact and bright within one to two minutes if a saturated solution of copper sulphate is mixed with ammonium oxalate so as to form the double salt, and a current of 1 ampère is passed through the liquid. The formation of the double salt should be effected in a beaker, and the hot clear liquid transferred to the platinum capsule. It is electrolysed with a current of $ND_{100}=0·5—1$ ampère, care being taken that the hot solution is always kept acid. For acidification we use a solution of tartaric acid (3 : 50). The metal is washed without interrupting the current. There were used from 1·8 to 2 grms. zinc sulphate, 4 grms. potassium oxalate, and 120 c.c. of liquid. The deposits were metallic, of a fine pale blue.

Iron.

The author used from 2·6 to 2·8 grms. potassium-iron oxalate, $Fe_2(C_2O_4)_3 3K_2C_2O_4+6H_2O$, and 6 or 7 grms. ammonium oxalate. The deposits were bright and metallic. The most favourable conditions for the precipitation of iron are $ND_{100}=1·5$ ampère and an ordinary temperature.

* *Berichte der Deutschen Chemischen Gesellschaft.*

Nickel.

The condition of the deposit is best on electrolysis in heat (60—70°), with a current of $ND_{100}=1$ ampère.

Cobalt.

In order to obtain fine metallic deposits the same conditions are required as for nickel.

Mercury.

The author used 0·4 to 0·41 mercuric chloride, 4 to 5 grms. ammonium oxalate, and 120 c.c. of liquid. The density of the current was 0·2 to 1·0 ampère, the tension at the electrodes 2·6 to 3·7 volts,, the temperature from 23° to 37°, and the duration from 5¼ to 1¼ hours.

Silver.

The author used 0·8 to 0·87 grms. silver sulphate, with 3 grms. of the purest commercial potassium cyanide to 120 c.c. liquid. In one experiment the author used pure potassium cyanide, obtained by passing hydrocyanic acid into alcoholic potassa. The weight obtained was in this latter case slightly larger. The deposit of silver is of a fine matt.

Tin.

There were employed from 0·9 to 1 grm. $SnCl_42NH_4Cl$ in 120 c.c. of a saturated solution of acid ammonium oxalate. The density of the current was at first 0·2 to 0·3 ampère, and was finally increased to 0·5.

When using larger quantities of it, it is necessary to add from time to time acid ammonium oxalate, in consequence of the decomposition of the acid ammonium oxalate and the setting up of an alkaline reaction. According to subsequent experiments, the determination of tin may also be effected by forming the double salt with neutral ammonium oxalate and acidifying with acetic acid. We add about 100 c.c. of a saturated solution of ammonium oxalate to the solution of the tin salt, and acidify with about 25 c.c. of acetic acid of sp. gr. 1·0615 (about 50 per cent). This procedure is especially to be recommended if the electrolysis has to be left to itself for a long time, *e.g.*, over night. The texture of the deposit, in contradistinction to that from the acid ammonium oxalate, is radiating crystalline. Tin adheres better to matt capsules than to such as are polished.

In the author's experiments the density of the current was increased towards the end.

Antimony.

As it is well known, relatively little antimony is firmly deposited on a polished surface of platinum, hence it is necessary to use only feeble currents. Under these conditions it requires from fourteen to sixteen hours. More recent experiments refer to the use of matt platinum capsules, as proposed by the author. Such capsules permit of the deposition of larger quantities, 0·6 to 0·9 grm. and upwards, and the use of strong currents, so that the determination of this metal can be effected in from two to three hours. The deposits of antimony had a metallic lustre. The metal was, in each experiment, washed without interrupting the current.

Lead.

The author has previously reported on the accurate deposition of the lead peroxide for the quantitative determination of the metal.

(To be continued).

A Misuse of Platinum.—Chemists and electricians will learn with dismay that an inventor has had the unhappy idea of using platinum in the manufacture of ladies' stays, and that a rise in its price may consequently be apprehended.

CONTRIBUTIONS TO THE CHEMISTRY OF CERIUM.*

By L. M. DENNIS and W. H. MAGEE.

(Concluded from p. 217).

IV.—*The Hydroxides of Cerium.*

THE peculiar colour changes of the hydroxides of cerium have often been noticed by chemists who have experimented with that element. When any one of the alkaline hydroxides is added to a solution of a cerous salt a white hydroxide is precipitated. This, so most authorities state, becomes slowly yellow on exposure to the air, more rapidly if chlorine or other oxidising agents be present. Popp (*Ann.*, cxxxi., 361), however, claims that he obtained a dirty violet hydroxide by leading chlorine into a solution of a cerium salt precipitated by an acetate. This he claimed to be a higher hydroxide than the yellow. He states that it gave on ignition a red oxide. Others have claimed that his violet hydroxide was a basic acetate. Rammelsberg (*Pogg. Ann.*, cviii., 45) obtained a like-coloured hydroxide by precipitating a hot solution of ceroso-ceric sulphate with caustic potash. Hermann (*J. Prakt. Chem.*, xxx., 189; xcii., 113) and Stapff (*J. Prakt. Chem.*, lxxix., 257) also obtained peculiar hydroxides, to which they attempted, without much success, to assign formulæ. Later, Lecoq de Boisbaudran (*Compt. Rend.*, c., 605), by the addition of ammonium hydroxide and hydrogen peroxide to a solution of a cerous salt, obtained an orange-red precipitate, which was studied by Cleve (*Bull. Soc. Chim.* [2], xliii., 57), who, as a result of his observations, considered it the hydroxide corresponding to an unknown CeO_3, namely $Ce(OH)_6$.

The following observations may throw some light upon the matter:—A solution of mixed chlorides, containing lanthanum, didymium, and cerium, was boiled and precipitated, while hot, with ammonium hydroxide. This was done in a large bottle which could be tightly corked. The mixed hydroxides were almost perfectly white, having possibly a faint pinkish tint. After the hydroxides had settled, the supernatant liquid was poured off, and the bottle was re-filled with thoroughly boiled distilled water. This was repeated until all foreign salts had been removed, the bottle being kept closely stoppered except while decanting and refilling. The hydroxides suffered no change of colour upon standing for some days. Therefore cerous hydroxide and the hydroxides of didymium and lanthanum when mixed are almost white. Didymium hydroxide by itself, however, or without much intermixture of white hydroxides, has a pinkish colour. Finally, air was blown through the suspended hydroxides. The colour rapidly changed, at first to a dull purple and finally to a pale yellow,

Next a solution of cerous chloride was treated in the same manner. The hydroxide remained perfectly white while air was excluded, but being exposed to air it took on a dull purple colour, changing later to a bright yellow. Through another similar sample, air freed from carbon dioxide was passed; the same change in colour resulted. Through yet another, pure carbon dioxide was passed. It remained white, and did not change to purple even when, after some time, air was substituted for the carbon dioxide, the stability doubtless being due to the complete transformation of the hydroxide to the carbonate. Through yet another sample, air from which both oxygen and carbon dioxide were removed, that is, nitrogen, was passed. It remained white. Next a bottle was about one-sixth filled with cerous chloride, and this was precipitated—white—with ammonium hydroxide, and the bottle was then filled with unboiled water and lightly stoppered. The precipitate changed in colour quite rapidly to light purple, which gradually became darker from above down-

* From the *Journal of the American Chemical Society*, October, 1894. Read at the Brooklyn Meeting, August 15, 1894.

ward, and finally the top began to change to yellow. After about four months the upper third had become yellow, that below it being still violet.

Both the white and the purple hydroxides, when washed on filter-paper, dried at a low temperature and then ignited, gave an olive-green oxide, which did not become yellow even when the highest heat of the blast-lamp was applied. On powdering it very finely it seemed more nearly yellow. The weights seemed to agree well, however, with that called for by ceric oxide. The yellow hydroxide, when dried and ignited, gave a pale yellow ceric oxide. When the yellowish-white oxide prepared by this method, or by igniting the oxalate, is again ignited over the blast-lamp, but in an atmosphere of hydrogen, it becomes olive-green without marked loss of weight. For example, 0·1263 grm. of yellow oxide ignited in hydrogen weighed 0·1261 grm.; 0·1574 grm. similarly treated gave 0·1570 grm. When again ignited in air or oxygen, the oxide became yellow and regained its original weight. Bunsen (*Ann.*, cv., 40) obtained very similar results.

As mentioned in a previous section, the precipitate obtained by the united action of ammonium hydroxide and hydrogen peroxide, on being dried and ignited, gives a pink oxide which seems to weigh somewhat more than ceric oxide, CeO_2, should.

Another point, perhaps worthy of notice, was that when some of the purple hydroxide was dissolved in sulphuric acid, and allowed to stand for a few days, there separated out a crystalline sulphate which, on analysis, gave results too high for cerous and too low for ceric sulphate.

It is to be concluded, then, so far as the present observations go, that cerous hydroxide is white; that on exposure to oxidising agents, including atmospheric air, it becomes first purple and then yellow, or, in other words, the purple hydroxide is an intermediate product.

ACTION OF LIGHT ON BACTERIA AND FUNGI.*

By Professor H. MARSHALL WARD, D.Sc., F.R.S., F.L.S.

The Italians have a proverb which runs, "*Dove non va il sole va il medico*"—Where the sun does not enter the doctor does—and which may be taken as an expressive summary of the experience of a people who have had opportunities of learning by many and varied trials how important for health is a due exposure to sunlight. Moreover, we find the same proverb, in almost the same form, in the Provençal dialect—"*Di lo mésou enté n'entro pa lou sonlé viebo lou médeci*"—and that this empirical recognition of the sanitary powers of sunshine is common to many nations, and everyone who has resided in India and the East knows how naturally the servants expose clothing and other articles to the direct rays of the sun.

In answer to the question, "Does the above proverb, and its equivalents in the languages of other peoples who have much to do with intense sunshine, really imply any knowledge or suspicion of the direct action of solar rays on organic materials or objectionable living beings?" we are no doubt justified in replying, No. If they have thought about the matter at all, the people have assumed that the heat of the sun's rays and the ordinary action of the air are the factors concerned; and that it is no doubt a sort of mixed effect of dryness and ventilation that is to be aimed at when they expose the interiors of dwelling-rooms, soiled clothing, and so forth to the process of being "aired," as they have it.

On the other hand, we find that experience of similarly varied and often bitter kind has also taught the children of sunny climates that the very brilliant sunshine which they so correctly extol as efficient in purifying their houses and apparel is a dangerous enemy to human beings who are unduly exposed to the direct solar rays. All the painful experience connected with snow-blindness, sunburn, and sunstroke may be invoked in support of this statement, and it requires but a careful study of this subject to be convinced that in these cases at any rate the effects cannot be put down to the mere heating power of the sun's rays.

Closer examination of the whole question drives us to the conclusion that the effects referred to and many other effects of direct insolation, are not due to the heat rays at all, but to actions of quite other kinds induced by rays long unsuspected of having anything like the hygienic importance they really have. But it has required much careful experimental investigation to decide this matter, and I propose to show you some of the principal steps in the chain of proof.

The fact that bacteria, which would multiply at an enormous rate in certain organic liquids, as, for instance, dilute meat broth, cease more or less evidently to do so if the fluid containing them is exposed to intense sunshine, was first pointed out by Messrs. Downes and Blunt in 1877 and 1878, and further experiments have abundantly confirmed their result. The establishment of this truth led to a more or less desultory controversy, turning on the question whether the effect was merely one of relatively high temperature, or whether it was really due to the light rays—in other words, whether those rays of the solar spectrum known to us especially by their thermal actions, induced the death of the insolated bacteria, or whether other rays of the solar spectrum were concerned.

This controversy was brought virtually to an end by the various experiments of Downes and Blunt, Arloing, Janowsky, and others, who showed that, in many cases at any rate, the bacteria in the tubes of broth, &c., were either killed outright, or rendered almost incapable of further development in ordinary daylight, or in tubes cooled by ice, or—in later experiments—in tubes behind screens which cut off the heat-rays to such an extent that no question of temperature could possibly be raised.

Meanwhile, another controversy arose, and was also carried on in a more or less disjointed manner through a series of years. This turned on the question—granted that the bactericidal effect is not due to high temperatures, may it not be merely the result of some poisoning effect of certain substances produced in the food-medium (broth, &c.) under the oxidising effect of the air in the illuminated tubes?

Duclaux was, I believe, the first to assert this definitely, and it was regarded by many as confirmed by experiments performed by Roux in 1887. It was pointed out that certain rays—more especially those towards the violet end of the spectrum, and known popularly as the "chemical" rays—are very apt to promote oxidative decompositions in solutions of organic substances, such as the broth used for cultivating these bacteria. It was also shown that the death of the bacteria in question did not result if all traces of oxygen are removed from the tubes previous to insolation. It had also been rendered at least highly probable—though there was as yet no agreement on this point—that certain rays of light only, some thought the red, others the blue-violet rays, are especially concerned in the process. The conclusion drawn, therefore, was that the effect was primarily due to a poisoning action of the broth or other food-material due to the energetic oxidations promoted in it by the solar rays when exposed to the light of the sun.

Meanwhile, other questions were being asked by those who were not satisfied with this explanation, or in the ordinary course of experimental inquiry into the subject.

It had already been decided that Downes and Blunt's experiments could not be accepted as conclusive, because they were not conducted with pure cultures, but with mixed infections of various bacteria, the growth or non-growth of which was decided merely by inspection of the turbidity or otherwise of the broth. Duclaux was one of

* A Lecture delivered at the Royal Institution of Great Britain, April 27, 1894.

the first to use pure cultures in 1885, and Arloing about the same period showed that some injurious effects on the spores could be induced by artificial light, such as strong gas-light, though it did not kill the bacteria.

Then Geissler, in 1892, came to the conclusion that the light from a powerful electric arc-lamp has some retarding action on the typhoid bacillus, though it was much feebler than direct sunlight, a result confirmed later by Chmelewsky, thus making it probable that the action of light on these organisms is merely dependent on the kind or intensity of the rays, and not on the source of the light.

But the most interesting controversy was that which had meantime arisen concerning which of the various rays of the spectrum are the really effective—or the most effective ones.

That the various rays of the solar spectrum act differently on plants has long been an established fact in botanical science, and the experiments of Famintzin, Batalin, Sachs, Pfeffer, Paul Schmidt, Naegeli, Pringsheim, Elfving, and others have put beyond doubt that it is of material importance to an ordinary plant not only whether it is excluded from or exposed to light, but also whether the light to which it is exposed contains the normal proportions of the various rays known to us in the visible and invisible spectrum, or is deficient in some of these.

To mention one or two illustrative cases only. The highly refrangible rays in the blue-violet region of the spectrum have a powerful effect on the processes of growth proper in a plant, and in heliotropic curvatures of the growing parts, whereas the process of carbon dioxide assimilation is chiefly dependent on the less refrangible red-orange rays at the other end of the spectrum. Again, the infra-red rays, if only in virtue of their thermic effects, are known to be of importance in growth, though in quite a different way from the rays above mentioned; while Sachs has given reasons for believing that the invisible ultra-violet rays at the other extreme of the spectrum have quite different effects again in the development of coloured flowers, and so on.

It was natural, therefore, to raise the question whether all, or only some, and if so which of the rays composing the solar light are effective in retarding and killing bacteria—especially when we remember that bacteria are plants—or at any rate that many of the organisms so denominated belong to the vegetable kingdom.

Two methods have been employed for the purpose of answering this question. The first, employed by Downes and Blunt, Arloing, Janowsky, Geissler, and Kotljar, was to use screens of coloured glass, or coloured solutions, &c., behind which tubes of broth or other liquids containing the bacteria were placed, and to judge of the effect by comparing how rapidly the broth became turbid; or behind which gelatin tubes, or agar or potato cultures were exposed, and a rough estimate made as to how well or ill the bacteria grew on the surfaces.

The second was to place such tubes in the various regions of the spectrum, and compare the results, as before, by judging of the turbidity of the broth, or the rate of growth on potato, &c., &c. This method was employed by Arloing, Janowsky, Chemelewsky, and Geissler.

Quite apart from other drawbacks to any such methods as these, and while fully recognising their historical necessity as pioneer work, it is obvious that no very accurate results could be expected from them, and as matter of fact we find up to 1892 that opinions were so divided on the question, Which are the effective rays? that no definite conclusion could be drawn. For instance, Arloing could not distinguish the action of any one particular set of rays from that of others, while Gaillard concluded that all the rays have a feeble effect. Santori concluded that neither the red nor the violet rays are the active ones, whereas Janowsky thought both the red and blue-violet were the effective rays.

Roux and Duclaux thought the action was due to a poisoning of the bacteria by products of oxidation of the food-medium, while Arloing and others insisted it was a direct action of the light. Some denied the facts altogether, or believed that all the light did was to retard the germination of the spores; while others insisted that the bacilli are more easily destroyed than the spores, and that it was all an obscure matter of temperature. In fact, previous to 1892, the utmost confusion existed, and all kinds of statements were current on the subject among the very small band of observers who concerned themselves at all with it; the best indications of the want of definite knowledge being, perhaps, the silence of the text-books on the matter.

The fact is that the methods in use up to that period were inadequate for the solution of the problems that had arisen, and many cautious bacteriologists were consequently sceptical as to the bactericidal effects of the sunlight, or indeed any light at all.

During the course of my investigations into the vitality of the anthrax bacillus when its spores are left in water, I was struck with the rapidity with which the bacillus disappears from tubes exposed to the sunlight, a fact often observed before, and recorded by Straus, Buchner, Momont, Frankland, and others, and usually supposed to be due to the spores germinating out into tender bacteria, which are then killed off. This is by no means the case, however, for the spores are themselves so acted on by the light-rays that they become incapable of germinating at all—they are *directly killed* by some injurious action set up in their interior by certain rays, and this at temperatures much lower than that we are now employing, *whereas these spores are not killed by mere boiling* for a minute or two, and will withstand *for hours*, and even days, temperatures *far higher than any they are subjected to in the experiments* I am going to describe.

In experiments where the spores of *Bacillus anthracis* were left in distilled water exposed to light for a few hours, it was found that many of the spores died, while of those which were left the germinating power was very much weakened. If, for instance, a number of spores were distributed in pure distilled water, and thoroughly shaken up, and the infected water was then divided into two portions, one exposed to light and the other not, every sample drop taken from the former tube was found to contain far fewer living spores than any sample drop from the latter. This confirmed the results observed by others, and already referred to—the sunlight in some way kills the spores, even in pure water.

It was further noticed that if I mixed a drop of the freshly-infected water with sterile gelatin or agar, and then poured the liquid transparent mass on a shallow glass dish, and allowed it to set or stiffen there into a transparent film, considerable differences were observable according as such a plate-culture was left exposed to the light or covered up from it.

In the latter case each of the numerous invisible spores contained in the drop of water, and now evenly distributed through the transparent mass of solidified gelatin, &c., germinated out in a few hours, and formed a colony of bacteria so dense and opaque that the previously clear gelatin, &c., became studded closely with them, and looked as if peppered over with a dense cloud of dust: whereas in the former case the light was found to have killed so many of the spores that only a very few colonies were formed on the plate at wide intervals, and separated from one another by the portions of transparent gelatin in which no growth had occurred.

[Plate-cultures shown illustrating this.]

It must be borne in mind that the gelatin, which remains transparent in this case, is just as richly charged with spores as in the other case, only the spores remain invisible owing to their minuteness; they are dead, and therefore cannot germinate and grow and develope into the colonies which render the gelatin, &c., opaque.

It was pretty obvious that if the light was the agent

which thus killed the exposed spores, the effect ought to be better brought out by exposing part only of the gelatin plate, and covering up the rest. This I did as follows, by a modification of a method long known to botanists, and practised by myself for years. A large quantity of spores was thoroughly shaken up in distilled sterile water, so that every c.c. of the water contained from 1,000,000 to 5,000,000 of the invisible spores. Then about five drops of this water was mixed with gelatin, warmed until quite liquid, and the whole rapidly poured in an even thin film over the flat floor of one of these thin clear glass dishes. In five or ten minutes the gelatin had set to a thin transparent film, containing say 5,000,000 invisible spores. The bottom of the dish, outside, was now covered with a zinc stencil-plate, through which a letter of the alphabet (say E) was cut, and every other part of the dish wrapped over with tin-foil and black paper, so that no light could reach the film except that which passed through the E-shaped opening in the metal stencil-plate in contact with the thin glass on which the gelatin film rests.

[Demonstration of method of making and exposing such plates.]

The plate, letter downwards, was then suspended over a plane silvered-glass mirror, placed at an angle such that the rays of the sun could be reflected up vertically through the letter, for two, three, or more hours.

After this process of exposure, the coverings and stencil-plate were removed from the plate, and the latter put in a warm dark incubator. The film showed no effects, but was still an even transparent sheet of gelatin, because the spores, dead or alive, are so minute that they in no way perceptibly interfere with the clearness of the gelatin, and none have had time as yet to germinate out.

On allowing such an exposed plate to remain, in the dark, at a temperature suitable for promoting the germination of the living spores, however, a marked and striking result is obtained in from twenty-four to forty-eight hours or so; for it is found that those spores which lie imbedded in the parts of the gelatin sheltered from the light, by the foil and other coverings, have germinated out normally and developed into visible colonies, which render the gelatin opaque, and which are so numerous that they run into one another, and so produce a general grey, white, or other coloured layer, according to the kind of bacterium, &c., used, whereas those spores in the E-shaped area exposed to light do not alter, because they are *dead*,—killed by the light,—and therefore do not affect the clearness and transparency of the gelatin, being invisible on account of their minuteness.

Consequently we see a transparent letter E picked out from an opaque matrix of growing bacteria.

[Photographs and plates shown.]

Buchner, by a method essentially similar to this, showed that a few hours' exposure to the intense light of the sun in summer suffices for this; but I showed that the much feebler rays of the winter sun are capable, even after reflection from a mirror, of totally killing the spores of the anthrax bacillus, at a temperature so low that even the gelatin ordinarily employed in cultures, and which runs at 29° C., is not melted. Since the spores employed will withstand very much higher temperatures — 55° C. to 60° C.—for many hours, it is clear that these experiments are conclusive against the supposition that the bactericidal action is due to the temperature. Having established this point for this and a number of other forms, including some mould fungi and yeasts, the next step was to settle the question whether the light action is really direct on the spores, or due to some poisoning action owing to products of oxidation of the food-materials.

This problem I attacked in the following manner:—Spores were shaken up in pure water, and the mixture poured into sterile shallow flat glass dishes,—the Petri dishes used for plate-cultures,—and dried there in a hot oven at 60° C. to 70° C., or even higher; this does not injure the spores, but renders them air-dry, and they stick as a thin powdery film to the bottom of the plate in this condition.

I then prepared several plates of agar films, sterile and without spores, and proceeded further according to the following argument:—If the solar action depends on the formation of some poisonous oxidation product in the agar, then, if I expose one of these sheets of agar, covered with a stencilled letter, to the sun, and then superpose it on an *un-exposed* film of the spores only, the latter ought to refuse to germinate on the letter-shaped area of the agar which had been exposed, whereas they should grow on the parts of the agar which had been protected from the sun.

But on trying the experiment such proved not to be the case. On the contrary, the spores germinated equally well *all over the agar film*, on the parts exposed as well as on those not exposed. In other words, the agar is not rendered in any way a worse pabulum for the spores by exposure to the sun's rays—a fact quite in accordance with numerous other experiments I tried.

This result by itself, however, is far less conclusive than when taken with the reciprocal experiment, as follows:—

Side by side with the sterile agar film above referred to, I also exposed a film of the dried spores—without agar—for the same period, and under the same conditions as to covering stencil-letter, &c. If, now, the solar action is direct on something in the spore itself, then those spores in that letter-shaped area of the film to which the stencil-plate allows the sun's rays to have access ought to be killed; consequently, on superposing a non-exposed film of agar on to one of these exposed films of spores, I ought to obtain a transparent letter after the spores around have grown out into opaque colonies. And such proved to be the case, as the photograph shows.

[Experiments and photographs demonstrated.]

These reciprocal experiments, taken together, conclusively show that the light-action is really direct on the spores themselves, and that the solar rays do not perceptibly affect the food-value of the agar films.

The same result is also obtained by taking some of the germinating spores from the non-exposed parts of a gelatin or agar plate in the previous experiment, and placing them on the exposed area where all the spores have been killed: they grow and flourish on this exposed area as well as they do on the non-exposed one, whence may be inferred that the bactericidal action, whatever it is, is not a mere consequence of poisoning from outside. It is evidently due to the light-rays directly inducing some changes in the substance of the spore itself.

The practical hygienic importance of this discovery is considerable, and would not be diminished even if it had turned out to be true that the light-action was really on something at the immediate surface of the spore; for it is clear that when spores escape into the air, and are exposed to the direct rays of the sun, they run exactly the risks I here subjected them to, and, as matter of fact, we find it is of the utmost importance in bacteriological investigations not to allow the spores of bacilli, fungi, &c. (even when fully ripe and otherwise fit for keeping in dry tubes, &c., for years), to be exposed to the light, for under such circumstances they gradually deteriorate.

Now we can see why it is so essential to health that our streets, houses, clothes, &c., should be thoroughly exposed to the sunshine. Moreover, as will be clearer in the sequel, these experiments render intelligible why it is that epidemics of parasitic fungi are so often connected in people's minds with dull, cloudy, sunless weather, and the Italian proverb with which I opened this lecture has for us a meaning far deeper and more significant than it had before.

(To be continued).

On some Salts of Hydronitric Acid. — MM. Berthelot and Vieille.—The salts examined are those of ammonium, N_3HNH_3, the tri-mercuric and tri-mercurous salts, N_6Hg (?) and N_3Hg.—*Bulletin*, xl.-xii., No. 15.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, October 26th, 1894.

Prof. A. W. RÜCKER, F.R.S., President, in the Chair.

THE meeting was held in the rooms of the Chemical Society, Burlington House.

In opening the proceedings, the PRESIDENT said the occasion might be regarded as another sign that the boundary between Chemistry and Physics was breaking down. On behalf of the Council, he tendered the thanks of the Physical Society to the Chemical Society for the use of the rooms.

Prof. H. E. ARMSTRONG, President of the Chemical Society, said his Council offered a cordial welcome to the Physical Society. The change, he thought, would prove of much greater importance than a mere removal. Now that the childhood of the Physical Society was passed, its manhood involved new responsibilities, and great opportunities for good presented themselves. The Physical Society of London ought now to become the head-centre of physics in the United Kingdom. He (Dr. Armstrong) was pleased to learn that the Society had undertaken the preparation and publication of abstracts of physical papers appearing in foreign periodicals, and said the matter was of such great importance that it should be done thoroughly. In a work of such a magnitude, he regarded the co-operation of other societies, such as the Institution of Electrical Engineers, as absolutely necessary.

The PRESIDENT, in acknowledging the welcome, said the Physical Society was extremely obliged to the President and Council of the Chemical Society for the great benefits conferred. Dr. Armstrong's advice, to go a-head, would not be forgotten. He then announced that at future meetings tea would be provided for members at 4.30.

The Exhibition of a Voltameter by Mr. Naber was postponed.

Mr. E. H. GRIFFITHS, M.A., read a paper on "*The Influence of Temperature on the Specific Heat of Aniline.*"

After pointing out that most observations of specific heat depend on water, whose capacity for heat varies considerably with temperature, the author said large differences existed between the values obtained by different observers as to the latent heat of evaporation of water and other liquids, and these differences were probably due to the variability of the water standard, which had been erroneously assumed constant. Precise measurements in calorimetry were of such great importance that the exact relation between the capacity for heat of water and its temperature should be completely determined. With apparatus such as he had used with aniline, this could be done in six months, provided someone could be found who could devote his whole time to the subject. The results of his own experiments were expressed in terms of the capacity for heat of water at 15° C. (at which $J = 4{\cdot}198 \times 10^7$ ergs), and hence were referred to a definite standard.

A great desideratum in calorimetric work was a calorimeter whose surroundings could be kept at a very constant temperature. This he had obtained by using a tank holding about 20 gallons of water, in which a steel vessel, shaped like a hat box, with hollow sides and bottom, was immersed. The cavity was filled with about 70 lbs. of mercury, and served as the bulb of a thermometer; a tube communicating with this bulb acted as a regulator to control the gas supply which heated the water in the tank. The tank water was circulated rapidly by a screw propeller. Under ordinary conditions the temperature of the outside of the steel chamber could be kept constant within $\frac{1}{100}$° C. The calorimeter itself was of brass, and suspended by glass tubes from the lid of the steel chamber. A stirrer worked by an electromotor kept the contents in rapid motion.

In the experiments on aniline, heat was supplied to the liquid in the interior by maintaining known potential differences (equal to some multiple of the E.M.F. of a Clark's cell) between the ends of a coil of German silver wire placed inside. The rate of rise of temperature of the inside over the outside was measured by platinum thermometers, one of which was placed in the calorimeter and the other embedded in the walls of the steel vessel surrounding the calorimeter. By this means differences in temperature of $\frac{1}{1000}$ of 1° C. could be detected with certainty. A special method of adjusting the potential differences between the ends of the German silver wire was employed by which the constancy could be maintained within 1 part in 10,000.

To minimise corrections arising from heat generated by stirring the liquid, and that lost by radiation, &c., from the calorimeter, the experiments were made about temperatures at which these corrections balanced each other; the rise of temperature was then due to the electric supply alone. The specific heat, S_I, of the liquid at temperature, θ_I, could then be determined from the formula—

$$\frac{d\theta_I}{dt} = \frac{E^2}{JR_I(S_IM + w_I)}.$$

Where,—

$\frac{d\theta_I}{dt}$ = rate of rise of temperature at temperature θ_I.
J = mechanical equivalent of heat.
E = potential difference between the ends of the coil.
R_I = resistance of the coil.
M = mass of liquid.
w_I = water equivalent of calorimeter at temperature θ_I.

Experiments were made with different values of E, and two widely different masses of liquid were used. The author was thus enabled to find S_I without knowing w_I. Having found S_I, the water equivalent of the calorimeter could then be determined.

Many important details of construction and manipulation of the apparatus, and the method of reducing the results, are given in the paper. The final values for S_I and w_I at several temperatures are given below :—

Temperature.	Specific heat of aniline.	Water equivalent of calorimeter.
15° C.	0·5137	79·82
20	0·5155	80·11
30	0·5198	80·90
40	0·5244	82·19
50	0·5294	83·39

The aniline employed was supplied by Messrs. Harrington Bros. as "pure colourless," but had initially a light brown tinge. After being in use some time, the colour had darkened considerably, but its specific heat had not sensibly changed. Recently he had tried a hydrocarbon liquid which promised to be still more satisfactory as a standard liquid in calorimetry. In the course of his remarks the author said a name for "capacity of heat per unit volume" was greatly needed, and invited suggestions.

Dr. ARMSTRONG thought the author had made a particularly happy selection in aniline, for it could now be obtained in almost any quantity absolutely pure. When pure it did not discolour on exposure, and would probably be very satisfactory as a standard liquid. He doubted whether any hydrocarbon could be better.

Prof. AYRTON congratulated the author on the extreme accuracy obtained. Recently he had arranged an experiment to determine the mechanical equivalent of heat by the electrical method, which gave very accurate results, without any corrections whatever being necessary.

Prof. S. P. Thompson thought the whole phraseology of specific heat required revising.

Prof. Perry agreed with Mr. Griffiths that a name for "capacity for heat per unit volume" was greatly needed, and Mr. Lucas suggested "heat density," but this was not satisfactory.

Dr. Sumpner said most text-books on physics attributed the advantage of the mercury thermometer to the low specific heat of mercury, whereas the capacity for heat per unit volume was the important factor.

Mr. Watson enquired to what temperature the alloy which the author had used to connect glass to metal had been tested?

The President said the paper was of great importance, because it dealt with the application of electrical methods to thermometry. The mercury thermometer had been quite superseded for work such as had just been described.

Mr. Griffiths, in reply to Mr. Watson, said the alloy had been used successfully between 10° and 62° C. It gave way at 71° C. He was glad to learn from Dr. Armstrong that aniline could now be got pure. Prof. Ramsay had written to say that he did not think that the slight impurities in ordinary aniline would have much effect on its specific heats.

Mr. Blakesley asked if aniline could be taken as pure if it did not change colour on exposure.

Dr. Armstrong, in reply, said, Yes; if the boiling-point was also constant.

NOTICES OF BOOKS.

The Manifold Uses of Salt. The Salt Union Ld., Northwich.

Salt is one of the necessities of life, but as we in England are so accustomed to a cheap and plentiful supply we are rather apt to overlook its great and universal importance. In the pamphlet now before us our attention is drawn to the great variety of uses we are constantly putting it to. Common salt is found in the blood to the amount of nearly ½ per cent, and this quantity is entirely independent of any surplus contained in the food and carried away in perspiration, &c.

An old Chinese torture (and they are an ingenious people on such matters) was to keep the victim entirely without salt; two to three weeks is stated to be the longest time a human being could live under such conditions. On the other hand, a well-known Siberian torture, even now practised in "Holy Russia," is to feed the victims on salted fish, with no water, until they can hold out no longer, and "confess."

Die Analyse der Weine. ("The Analysis of Wines.") By H. A. Blücher. With 13 Woodcuts. Kassel: Max Brunnemann. 1894.

Wine-making in Germany is an industry of great national importance, and the Germans—with the methodical care which has for so long distinguished them—many years ago recognised that it is by minute attention to detail that the best results are obtained. In making wine, as much, if not more, care is required as in any other manufacture; the grapes should be selected and sorted, so that good bunches should not be contaminated with those of poorer quality, and, above all, careful supervision is needed during the period of fermentation or incubation of one of the useful microbes on which we are so dependent.

In these pages the author gives the latest methods for carrying out the various operations necessary for controlling the manufacture, and includes a large number of tables of results, as well as reduction tables used for simplifying the calculations.

CORRESPONDENCE.

DETERMINATION AND DETECTION OF COPPER.

To the Editor of the Chemical News.

Sir,—If Mr. John Spiller will refer to the fifth edition of "Fresenius's Quantitative Chemical Analysis," German edition, p. 281, footnote, he will see his question answered as follows:—

"Brown, who published the same method once more as novel (*Quart. Journ. of the Chem. Soc.*, x., 65), appears to have no knowledge of the publication in 1854. The small modification, consisting in determining the liberated iodine by means of hyposulphite (according to Schwarz), instead of by sulphurous acid (after Bunsen), is already contained in "Mohr's Volumetric Analysis," i., 387, published in 1855."

Fresenius states that the method was worked out in his laboratory by de Haen.—I am, &c.,

Otto Hehner.

DETERMINATION AND DETECTION OF COPPER.

To the Editor of the Chemical News.

Sir,—In the Chemical News (vol. lxx., p. 221) Mr. John Spiller, actuated by a most laudable feeling, makes a claim in favour of the late Mr. E. O. Brown for priority of the process for estimating copper based on the action of potassium iodide, and the titration of the iodine set at liberty.

This process is really due to De Haen, who published it in 1854 (*Ann. der Chemie und Pharmacie*, xci., p. 237), while Brown's work only dates from 1857 (*Quart. Journ. Chem. Soc.*, x., 65). I send this solely on account of the historical interest of the question.—I am, &c.,

Dr. L. L. de Koninck.

University of Liège, Nov. 4, 1894.

ESTIMATION OF CARBONATES AND CAUSTIC ALKALIS IN MIXTURES.

To the Editor of the Chemical News.

Sir,—My attention has been drawn to a correspondence (Chem. News, vol. lxx., p. 209) *re* my above article which appeared on p. 166, and I have in answer to state that I still give the preference to my method for accurate results, and I still maintain that other methods are erroneous.

It is a pity that Mr. J. A. Wilson has not the details of his past experiments with him, so as to publish them, and not to allow me to pass "unchallenged," as he terms it, but I should suggest that it would be worth his while to try the experiments again after such a lapse of time as "years ago," which has passed between his experiments and now.

Phenolphthalein as indicator was meant originally to be used only for organic acids, &c., and not for carbonates, and although it is largely used as an indicator for both, it is found very unsatisfactory up to the present.

Carbonate of soda alone gives an immediate colouration with phenolphthalein; if the other methods were correct, carbonate of soda alone ought not to give any colouration. The estimation of carbonates and caustic alkalis in mixtures, according to Mr. J. A. Wilson, means, as I said in my article, taking the total alkalinity with methyl-orange, and afterwards, on a second portion, with phenolphthalein, thus indicating the caustic soda originally present; the amount of carbonate being obtained by the difference between the total alkalinity and the alkalinity indicated by phenolphthalein in the second portion, because carbonate of soda, according to Mr. J. A. Wilson, does not give any colouration with phenol-

phthalein; but I find it does so. Hence the error.—I am, &c.,

P. L. Aslanoglou.

ESTIMATION OF CARBONATES AND CAUSTIC ALKALIS IN MIXTURES.

To the Editor of the Chemical News.

Sir,—With reference to Mr. J. A. Wilson's letter, *re* Mr. Aslanoglou's condemnation of phenolphthalein as an indicator, I may state that "years ago," at St. Thomas's Hospital, we abandoned that agent as untrustworthy and deficient in delicacy. With a gasometric apparatus the actual determination of CO_2 is easy, rapid, and far more reliable, bearing out Mr. Aslanoglou's statements.—I am, &c.,

C. G. Stewart,
late Demonstrator of Chemistry,
St. Thomas's Hospital.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. xi.-xii., No. 15.

Barium Nitride.—MM. Berthelot and Matignon.—Barium nitride was prepared by decomposing solution of ammonium hydronitride by an equivalent weight of baryta dissolved and evaporated *in vacuo* in the cold. The solution-heat for 1 mol. = $N_6Ba = 221 - 7{\cdot}8$ cal.

Methylenic Ethers obtained by the Action of Trioxymethylene and Ferric Chloride upon Alcohols.—MM. Trillat and Cambier.—This lengthy paper does not admit of insertion in the space at our disposal.

Rotatory Power of Amyl Pyruvate and Lactate.—L. Simon.—The author refers to the remarkable observations of Guye, *i.e.*, the influence exerted upon the rotatory power by the number of radicles combined with the asymmetric atom of carbon. Most, if not all, the acids of this group have very feeble rotatory powers. On the contrary, the lactones or lactonic acids have high rotatory powers.

Action of Thionyl Chloride (Chlorosulphurous Acid) upon Mineral Acids.—Ch. Mouren.—Thionyl chloride reacts in the cold upon sulphuric acid, liberating HCl and SO_2, and forming sulphuric monochlorhydrine and pyrodichlorhydrine. With nitric acid, thionyl chloride produces at first azotyle chloride. Then the hydrochloric acid formed, with nitric acid in excess, gives rise to the substances forming aqua regia; at the same time the sulphurous acid is oxidised to sulphuric acid. If orthophosphoric, metaphosphoric, and boric acids are heated with $SOCl_4$ to ebullition, they are immediately attacked, with escape of gaseous sulphurous and hydrochloric acids. The action upon metaphosphoric acid is limited by the points of contact. With orthophosphoric and boric acid there are soon formed chloro-products of condensation, which he thionyl chloride does not attack.

On Triacetylgallic Acid.—Hugo Schiff.—The author shows that the researches of Sisley and Bietrix have been anticipated by his own work, published in the *Bull. Soc. Chim.*, xv., p. 5.

On the Organic Matters constituting Vegetable Soil.—M. Berthelot and G. André.—The humic principles extracted from soils possess properties similar to those of artificial humic acid, especially as regards their aptitude to form insoluble potassium compounds resisting the action of natural waters.

New Researches on the Fixation of Atmospheric Nitrogen by Micro-organisms.—M. Berthelot.—The author shows the intervention of micro-organisms in the fixation of nitrogen.

New Researches on the Micro-organisms of the Soil which Fix Nitrogen.—M. Berthelot.—The author's results, which are given in a series of tables, and which are very decisive, have received a striking confirmation by the researches of Winogradsky. This *savant* has obtained a large bacillus which determines the fixation of nitrogen in media previously free from that element.

Studies on the Formation of Carbonic Acid, and the Absorption of Oxygen by Leaves detached from Plants.—M. Berthelot and G. André.—This extensive memoir does not admit of useful abstraction.

Remarks on the Heating and the Spontaneous Ignition of Hay.—M. Berthelot.—The increase of temperature which determines the spontaneous ignition of hay results from purely chemical reactions, which bear upon products modified at first by fermentations.

Revue Universelle des Mines et de la Métallurgie.
Vol. xxvii., No. 3.

On a Safety Lamp with a Standard Hydrogen Flame for the Recognition of Fire-damp.—Frank Clowes.—A translation from an English paper.

MISCELLANEOUS.

The Royal Society.—The following is the selected list of the new Council of the Royal Society, to be ballotted for Nov. 30th:—

President—The Lord Kelvin, D.C.L., LL.D.
Treasurer—Sir John Evans, K.C.B., D.C.L., LL.D.
Secretaries—Prof. Michael Foster, M.A., M.D.; The Lord Rayleigh, M.A., D.C.L.
Foreign Secretary—Sir Joseph Lister, Bart., F.R.C.S.,
Other Members of the Council—Andrew Ainslie Common, LL.D.; William Crookes, F.C.S.; Francis Darwin, M.A.; Andrew Russell Forsyth, Sc.D.; Sir Douglas Galton, K.C.B.; Prof. Alexander Henry Green, M.A.; Sir John Kirk, K.C.B.; Prof. Horace Lamb, M.A.; Prof. Edwin Ray Lankester, M.A.; Prof. Alexander Macalister, M.D.; Prof. John Henry Poynting, D.Sc.; Prof. Arthur William Rücker, M.A.; Osbert Salvin, M.A.; Prof. J. S. Burdon Sanderson, M.D.; Thomas Edward Thorpe, Sc.D.; William Henry White, C.B.

School Medical Officers.—In an article in the *Deutsch. Vierteljahrsch. f. Offenth. Gesündheitspf.* Dr. A. Spiess, Medical Officer to the City of Frankfort-on-the-Maine, gives his views on this question. In his own city Dr. Spiess also performs the duties of school medical officer. He is of opinion that in all towns the appointment of such an office is necessary. He should have a seat and a voice in the school committee, and should seek whilst in association with them to bring them over to his views. His periodical school visitations, which are indispensable, should always be made after notifying the master of his intention, and to the master alone should his observation be communicated. The most important part of medical supervision of schools is the continued joint action of the physician with the school authorities. Along with this is the periodical supervision of all sanitary work carried out in connection with schools. A school medical officer must not only be possessed of thorough general hygienic training, but must be specially conversant with school hygiene.—*Medical Press.*

[The presence of a medical officer having a seat and voice is necessary in every School Board, as so many of the members are ignorant and heedless of the vital conditions affecting the children.]

Catalogue of Modern Forms of Platinum Utensils and Apparatus. — Messrs. Baker and Co., of Newark, N.J., have just issued a very useful little catalogue of the most modern forms of platinum utensils and apparatus. Chemists of experience have, of course, no difficulty in deciding what platinum apparatus to get and where to get it; but younger men, and above all those who have not had the run of a large and well-furnished laboratory, are often at a loss to know exactly what they want, simply because they have never seen it. This Catalogue, fully illustrated, supplies this want, and also gives some useful hints on how to preserve and clean platinum; sodium amalgam possesses the property of wetting platinum without amalgamating with it. It is therefore useful for effecting a quick and thorough cleansing of platinum. The amalgam is gently rubbed upon the metal with a cloth, and then moistened with water; this oxidises the sodium, and leaves the mercury free to alloy with the foreign metals. The mercury is then wiped off, and the crucible polished with sea-sand in the usual way.

MEETINGS FOR THE WEEK.

THURSDAY, Nov. 15.—Chemical, 8. "The Alkaloids of *Corydalis Cava* (I. Corydaline, Part IV.; II. Corybulbine), by Prof. J. J. Dobbie and A. Lauder. And other papers.

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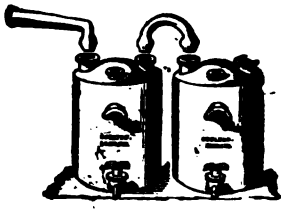

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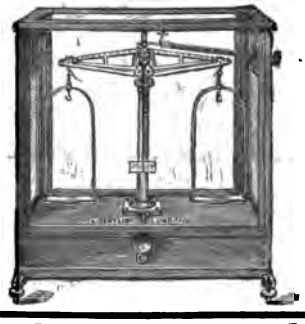

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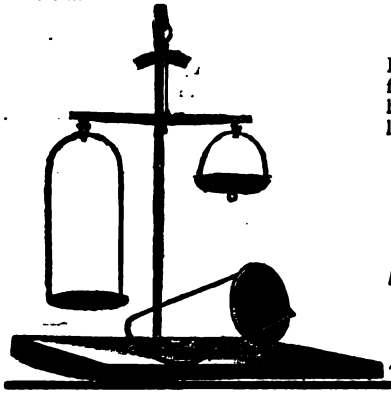

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THE CHEMICAL NEWS.

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THE POSITION OF MAGNESIUM IN THE GENETIC SYSTEM OF THE ELEMENTS.

By C. T. BLANSHARD, M.A.

MAGNESIUM shows many analogies with the natural group of elements—zinc, cadmium, and mercury; but from at least three important points of view of physical characters, which closely agree with each other, this element should rather be classed as the first of the lateral series including calcium, strontium, and barium; and this irrespective of several well-known chemical analogies with the latter metals.

First, to take the case of the important factor in classification, *atomic volume*.

This has been shown to have several other physical properties dependent on it; thus, *melting-point* was shown by the late T. Carnelley, who did much valuable work in this subject, to be closely related to atomic volume (*Phil. Mag.*, [5]. viii., p. 308); whilst Bettone (*Pogg.*, cl., p. 644) showed that *hardness* is similarly closely related.

If we take the atomic volumes, as calculated from the most recent and trustworthy authorities, of the dyad metals of the even series, generally taken together as a natural group, we have—

	At. vol.	Authorities. At. wt.	Sp. gr.
Magnesium	$\frac{24\cdot287}{1\cdot74} = 13\cdot9$	Burton and Vorce.	Bunsen.
Zinc	$\frac{65\cdot34}{7\cdot10} = 9\cdot2$	Gladstone and Hibbert.	Rammelsberg.
Cadmium ..	$\frac{111\cdot802}{8\cdot55} = 13\cdot0$	Partridge, Clarke.	Schröder.
Mercury ..	$\frac{200\cdot36}{13\cdot596} = 14\cdot7$	Erdmann and Marchand.	Regnault.

The atomic weights are referred to O=16. The specific gravities are taken at 0° C.

Here magnesium is evidently out of place. I hope to show later on that there are no anomalies in atomic volumes of natural groups; but that apparent anomalies can always be rectified by taking some allotropic form of the element under consideration.

Secondly, an analysis of the spectra of the dyad metals leads to the same conclusion as does the atomic volume.

To make the agreement more striking I put the figures in parallel columns. By an analysis of the spectra of various elements, considered in their natural groups Messrs. H. Kayser and C. Runge (*Ann. Phys. Chem.*, [2], xlii., p. 302, and xliii., p. 385) find, using for their calculations a modification of Balmer's formula, viz., $\lambda^{-1} = A + Bn^{-2} + Cn^{-4}$, the following values for A_1 and A_2. Here n is a whole number, which may vary from 3 to 16.

Dividing the group so as to place magnesium with calcium, we have—

Group II.—

Element.	At. vol.	A_1.	A_2.
Beryllium	4·9	—	—
Zinc	9·2	42945	42955
Cadmium	13·0	40755	40797
Mercury	14·7	40159	40218

Group II.*a*—

Magnesium ..	13·9	39796	39837
Calcium	25·6	33919	34041
Strontium	33·9	31030	—
Barium	36·5	—	—

Authorities.

	At. wt.	Sp. gr.
Beryllium ..	Nilson and Pettersson.	Humpidge.
Calcium ..	Erdmann and Marchand.	Matthiessen.
Strontium ..	Dumas.	Matthiessen.
Barium ..	Dumas.	Kern.

Thirdly, we have further corroboration of this place for magnesium in what W. Preyer ("Das Genetische System der Chemischen Elemente," Berlin, 1893) terms the *volume-heat*.

$$\text{Volume-heat is } \frac{\text{at. heat}}{\text{at. volume}} = CW \div \frac{W}{D} = CD,$$

where C is the specific heat, D the density of the element.

Taking the groups as before, we have—

Group II.—

Element.	Sp. heat.	Sp. gr.	C.D.
Beryllium	0·424	1·85	0·784
Zinc	0·0915	7·10	0·650
Cadmium	0·055	8·55	0·470
Mercury	0·0331	13·596	0·448

Group II.*a*—

Magnesium ..	0·245	1·74	0·426
Calcium	0·1804	1·57	0·283
Strontium	—	2·54	—
Barium	—	3·88	—

The specific heats quoted are taken as near 15° C. as possible.

Authorities for Spec. Heats.

Be	Nilson and Pettersson.
Zn	Naccari.
Cd	Lorenz, Naccari.
Hg	Naccari, Winkelmann.
Mg	Kopp, Lorenz.
Ca	Bunsen.

The values quoted are from Landolt and Börnstein, "Phys. Chemische Tabellen," 1894, or from more recent sources. To set against these three concordant results we have the fact that, by its *atomic heat*, this element can only be placed between beryllium and zinc.

This fact of *cross analogies*, as I beg to term them, will, it seems to me, make the solution of the question of the genesis of the elements a more difficult subject than would be at first supposed. In another article I hope to give the *volume heats* of the elements, and the laws that govern them,

AN ELECTRIC FURNACE FOR THE LECTURE-TABLE.

By H. N. WARREN, Research Analyst.

THE reduction of the refractory earths, such as alumina, glucina, &c., or a quick manufacture of small quatities of their alloys, must have often been a question of serious drawback to demonstrators whom the oxhydrogen flame refused to satisfy.

The above novel contrivance is now being supplied by the author to most of the leading universities; it consists, so far as the furnace is concerned, of an outward jacket of caloric cement, through the bottom of which passes a plumbago tube, while a rod of the same material is inserted through the top of the furnace, and so regulated as

to allow of the arc produced to play upon the compound placed in the cavity. Connected to the furnace is a small plant of special construction, and capable of evolving a voltage of 100° intensity, or can be readily arranged for amperical value, as required. Nearly every substance brought within the cavity is at once reduced, and a corresponding button of metal obtained; the furnace being also arranged with a side communication, whereby a small arc is obtained for the reduction of minerals. In this instance the mineral to be tested is first finely ground, and made into a paste with solution of pyroxylin, and afterwards rolled into a small stick; on bringing the same into contact with the flame from the carbon-points, reduction at once takes place, with the production of a metallic bead; the electric plant is also arranged entirely automatic, and the furnace can be put in action instantaneously.

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THE SIGNIFICANCE OF NITRITES IN POTABLE WATERS.

By P. L. ASLANOGLOU.

It may be as well to first consider briefly some of the properties of nitrous acid. Although these are generally well known, yet the behaviour of the acid and its salts in very weak solutions does not seem to have been much studied. I am undertaking some experiments on this point.

Nitrous acid, HNO_2, is of course the anhydride of nitrogen trioxide, N_2O_3, and easily breaks up by heat into the latter and water:—

$$2HNO_2 = N_2O_3 + H_2O.$$

But N_2O_3, except in the liquid state, is very unstable; when water is added, or very slight rise of temperatnre causes vigorous effervescence in forming nitric oxide and nitric acid:—

$$H_2O + 3N_2O_3 = 4NO + 2HNO_3.$$

But the decomposition is not complete; a quantity of nitrous acid is left. In more dilute solutions nitrous acid is more stable. In some of its reactions, such as the familiar test with acidified potassium iodide and starch, it acts as an oxidising agent; in others, such as those with silver nitrate and with permanganate, it is reducing; in yet a third class, such as those with organic substances like metaphenylene diamine, &c., it forms nitroso-compounds of intense colours, or breaks down amido-compounds into azo- or hydroxy-substances, as in phenylamine, liberating both nitrogens:—

$$C_6H_5.NH_2 + HNO_2 = C_6H_5.OH + H_2O + N_2.$$

A similar reaction is well known to occur on elevation of temperature with ammonia itself:—

$$NH_3 + HNO_2 = NH_4NO_2$$
$$NH_4NO_2 = 2H_2O + N_2.$$

We have here possibly the explanation of the fact observed by Messrs. Jordan and Richards:—"*Bacillus denitrificans*," both in the A and B varieties, reduces nitrates to nitrogen gas. The ammonia might be absorbed from the atmosphere, but this point requires elucidation. The direct conversion of nitric acid into ammonia requires the absorption of 4 atoms of oxygen:—

$$HNO_3 + H_2O - 4O = NH_3.$$

This is not very likely to occur without the intermediate formation of nitrous acid, which these authors, however, could not detect at any point.

Nitrites are more stable. They are alkaline, and are easily decomposed by even weak acids, setting free the nitrous. They absorb oxygen from the air, giving nitrates. I am attempting to elucidate—

1. How long nitrous acid and nitrites in very weak solutions, as in waters, take to be oxidised by free oxygen.
2. Whether very dilute nitrites are decomposed by carbonic acid. If they are, it follows that the nitrous acid in natural waters should be present in at least partially free state.
3. Whether and under what circumstances metals, such as iron, zinc, or lead, can reduce nitrates to nitrites; also the action of ferrous hydroxide.
4. The stability of ammonium nitrite in absence or oxygen. This presents considerable difficulty, as the solutions must be very dilute and must be cold at the beginning.

Dr. E. Frankland has always emphasised that the occurrence of nitrates indicates that the water is undergoing or has undergone a natural purification, and the quantity of nitrates found frequently denotes the proportion of nitrogenous organic matter destroyed; so much so that in his water reports he denominates the oxidised nitrogen (that existing as nitrates and nitrites) as previous sewage contamination. But it has been pointed out that in the case of deep well waters, which generally contain a notable quantity of nitrate, this contamination must have been geological, or derived from fossiliferons strata, and the purification must in the course of ages have been so complete that nearly all the carbonaceous matter has been removed as carbonic acid. Also, that in rain water the nitrate is of atmospheric or inorganic origin. Hence the significance is of very limited application, and may be delusive. Dr. Frankland himself observes, whether or no the analyst should form an unfavourable opinion of the water from the amount of nitrates must depend upon the proportion of organic matter present. The same authority observes that upland surface-waters are commonly free from nitrates and nitrites, or contain but a mere trace. In them the range of nitrogen in this form is from *nil* to 0·05 part per 100,000, with an average of 0·009.

The Artesian waters of the Kent Company contain 0·25 to 0·4; the Thames and Lea water companies 0·1 to 0·25. The range in well, surface, and spring waters is very wide, extending from *nil* to 5 or 10 m.grms. per 100,000. It is affected by—

1. The presence of free oxygen and the exposure to the air.
2. The presence or absence of reducing metals.
3. The number or character of nitrifying organisms.

As to the significance of nitrites very little has been said. It was formerly considered sufficient to test qualitatively for their presence, in default of good processes for their estimation, but of late years it has become increasingly customary to determine the amount volumetrically by the delicate colour methods. Dr. Frankland only says it is very rarely necessary to distinguish between nitrites and nitrates in water. Nitrites when present in water are soon oxidised to nitrates. The inference to be drawn from the presence of nitrites depends upon the source of the water. The presence of these salts in spring and deep well waters is absolutely without significance; for although they are in these cases generated by the deoxidation of nitrates, this deoxidation is brought about either by the action of reducing mineral substances, such as ferrous oxide, or by that of organic matter which has either been embedded for ages in the water-bearing stratum, or, if dissolved in the water, has been subjected to exhaustive filtration. In such waters the presence of nitrites has no more bearing on their wholesomeness than the absence of dissolved oxygen, which is characteristic of the most excellent waters from deep wells. When, however, nitrites occur in shallow, well, or river waters, it is highly probable that these waters have been very recently contaminated with sewage, for it seems that in the ordinary oxidation of sewage (which contains much ammonia, but no nitrates) by percolation through porous earth, its nitrogen is at once oxidised to the maximum,

nitrites being absent from effluent water of intermittent sewage filters, for instance. But when fresh sewage is added to water already containing nitrates, the latter are generally reduced to nitrites. It is much to be desired that the origin of nitrites in these classes of waters should be more thoroughly investigated.

Mr. G. Menoll, in 1875, first observed that well-water containing nitrates and also bacteria, on standing in a closed vessel for a week or a fortnight, showed, with acetic acid, potassium iodide, and starch, a distinct reaction for nitrites. Phenol, salicylic, or benzoic acid, prevented this effect. The addition of carbohydrates, and still more that of a little peptone, or of the ingredients of M. Pasteur's solution, accelerated the action. Various organisms were tried.

Messrs. Reichardt and Strohl remark that, inasmuch as spring water very rarely contains any nitrite, its presence in more than traces is a proof of external contamination. They draw attention also to the therapeutic action of nitrites in daily small doses.

Mr. Joseph Prestwich, in the case of the North Hinkley Spring, showed that sewage contamination from houses was here impossible, and that the nitrates and nitrites must be derived from the cultivation of the land. Even if this were conceded, it admits the presence of surface drainage, and admixture of recent manure might easily convey diseases from animals. It would be necessary to enquire whether the nitrates had been derived from a chemical manure applied to the land.

Mr. A. A. Ferreira pointed out that waters charged with nitrates and nitrites are very injurious to man, were yet conspicuously nourishing to vegetation, thus drawing attention to the purifying action of the latter.

Mr. H. Fleck says that a water for drinking must not contain a trace of nitrous acid; Mr. Sydney Gibbons considered the absence of nitrates and nitrites a matter for gratulation; while Mr. Wanklyn was of opinion that presence of abundance of nitrites does not show defilement by sewage, and deficiency of nitrates does not show absence of defilement.

Mr. Francis Sutton observes, it sometimes happens that when the supply of atmospheric oxygen is deficient the organic matter in water is oxidised at the expense of the nitrates present, and occasionally, if the quantities happen to be suitably proportioned, they are mutually destroyed, leaving no evidence of pollution.

We may take it as decided that the presence of nitrites indicates either—

1. The incomplete oxidation of nitrogenous matter and of ammonia; hence the probable occurrence of a recent contamination; or—
2. The partial reduction of previously existing nitrates by organisms like *Bacillus denitrificans*, or by reducing metals or oxides.

In any case their presence is an element of suspicion, and has to be accounted for; moreover, it is distinctly indicative of a deficiency of oxygen, which is a bad feature, as it renders the water less able to destroy any dangerous organisms which at any time may enter.

It has been stated on many occasions that nitrites are innocuous. This is certainly an error. Even such small quantities as are met with in waters may, in constant use, eventuate in a deleterious effect. That the accompanying absence of oxygen must have some injurious effect on digestion is rendered probable by the natural repugnance to waters that are flat, and by the fact that water artificially charged with the gas has been shown to have a beneficial effect in dyspepsia.

It has long been known that nitrogen trioxide combines with the colouring-matter of blood, giving it a darker colour and rendering it unfit to perform its functions; nitrites also, mixed with freshly drawn blood, give it a chocolate colour, and cause it to exhibit the spectrum of methæmaglobin. As the oxygen in the latter is more firmly combined with it than in hæmaglobin, substances such as the nitrites interfere with internal respiration; hence reducing substances accumulate in the blood; and methæmaglobin becomes reduced by the nitrites to the normal reduced hæmaglobin of venous blood. When this reaches the lungs it takes up oxygen, forming arterial blood, by which respiration is restored; thus, unless new supplies of nitrites are constantly added, the asphyxia quickly passes away. In drinking water, though the quantity is minute, this constant action would evidently occur, and might easily in time conduce to an anæmic state.

In 1883 Dr. Brunton administered to a number of persons 10-grain doses of pure sodium nitrite. Intense discomfort and graver symptoms of poisoning rapidly followed, so that the experiments could not be continued. Even 5 grains in some cases caused toxic results; 1 or 2 grains was badly tolerated—these were single doses. No report is given as to the effect of long-continued much smaller doses. Nitrites cause a fall of blood pressure, and depress and paralyse the capillary circulation, so causing cold at the extremities.

Messrs. Sydney Ringer and William Murrell say that sodium nitrite is a powerful toxic agent. Messrs. Binz and Barth first noticed the poisonous effects. Mr. Reichert states that holmic respiration is seriously interfered with, and tissue metamorphosis diminished. Nitrates are far less active.

Ten grains of sodium nitrite is the poisonous dose; even 2 grains cause blueness of the lips, headache, and giddiness.

It would be idle to calculate the amount of water that would be required to furnish a poisonous dose of nitrite; it is simply maintained as probable that their constant ingestion must have an injurious action in time.

What happens in polluted waters in contact with soil is this:—The putrefaction of organic matters of most kinds is complete in about seven days, as shown by the free ammonia no longer sensibly increasing. In fourteen days the ammonia has disappeared, and nitrite has taken its place, reaching a maximum in twenty-one days. Later, the nitrite also disappears if oxygen be present, and in twenty-eight days, or more, all the nitrogen has been converted into nitrate. Hence the purifying action on sewage of irrigation, and filtration through land.

It was for a long time supposed that a number of bacteria had the nitrifying power. Mr. Heroens cultivated about fourteen species in ammoniacal solutions, and obtained tests for nitrous acid from *Bacillus prodigiosus*. Mr. Finkler-Prior, typhoid, anthrax, &c. But Mr. Percy Frankland and others failed to find this, proving also that very few waters were free from the nitrifying organism, and that the more complete the nitrification, the fewer the bacteria in the effluent. At last Messrs. Percy Frankland and Winogradsky, independently, discovered the organism, describing it as humerous characteristic bacilli, hardly longer than broad, and giving the microscopic measurements. The earlier failures were due to the fact that *Bacillus nitrificans* will not grow in gelatin. Jordan and Richards describe it as short, slightly oval, grouped in irregular clumps, and held together by a jelly-like material (Zoogloea).

Subsequent investigations proved that there were several varieties of the organism; that of Messrs. Frankland and Winogradsky oxidises to nitrite, but no further; whereas Messrs. Jordan and Richards's variety, or species, gives complete oxidation to nitrate. Still other species, called by the latter observers *B. denitrificans*, A and B, actually reduce nitrates to nitrites. Any or all of these may be naturally present in waters and in soils. In water-logged soils they are specially abundant, the reducing species predominating; hence these show a larger proportion of nitrites.

It is remarkable that these organisms appeared to be capable of living and multiplying in water that seemed to chemical analysis to be free from any trace of organic carbon and nitrogen, thus apparently subsisting entirely on inorganic compounds. But it is much more probable

that such minute quantities of organic matters were present as had eluded the analysis.

Photographic illustrations of the nitrous and nitric organisms are given in the *Bulletin of the Rothamsted Experimental Station* (No. 8, 1891, Plates VI., VII., VIII.), by Mr. Robert Warington, F.R.S.; also in his papers in the *Journal of the Chemical Society* (1878-9, 1881-4-7-8, and 1891). "On Nitric Acid in Rain Water," *Ibid.* (1889, p. 537). "On the Action of some Specific Organisms on Nitric Acid," by Mr. P. F. Frankland, *Journ. Chem. Soc.* (1888, p. 373).

The investigation first establishing the action of the nitrifying ferment is due to Messrs. Schlœsing, of Muntz, but the actual organism was not separated and identified till long afterwards. No nitrification takes place in dry soils, the organism being killed by drying.

Earlier than this Mr. Schlœsing had found that the decomposition of nitrates during fermentation of tobacco-juice and beet-syrups, also when small quantities of wine were present, yielded nitrous and nitric oxides; that it did not occur in acid liquids, but only when the solution became neutral or alkaline; and that it often proceeded with such activity that all the nitrate disappeared in a few days.

It must be remembered that if this action occurred in waters either with nitrites or nitrates, Schlœsing and others at that time seem not to have noticed the formation of nitrites, the nitrous oxide would not be evolved as gas, as it is comparatively soluble, and nitric oxide, if any oxygen were present, would undergo re-oxidation, and would simply take up its usual *rôle* of a carrier of oxygen to the organic matter.

Messrs. Dumont and Crochetelle proved the favourable influence of potassium salts on nitrification. Salts of potassium are characteristic of sewage, in so much that the presence of potassium salts in natural waters raises a suspicion of sewage contamination.

Nitrites may be derived from manures. Nitrate of soda put on land is reduced in water-logged soils to nitrite. Mr. Robert Warington remarks that most natural waters are in themselves nitrifying when polluted with sewage.

Darkness is more favourable than light to the nitrifying ferment; a strong light stops its action. Nitrification does not take place in the absence of phosphates, as they are necessary for the food of the organism. A base such as carbonate of lime must be present. Experiments carried out by Messrs. Lawes, Gilbert, and Warington at Rothamsted farm in 1885 showed that the nitrifying organism is mainly confined to the surface soil, and occurs rarely and to a small extent in a clay soil at depths below 2 or 3 feet. In lighter soils it is formed deeper, but in no case below 6 feet.

Urea, albumenoids, &c., are easily nitrified, ammonia or ammonium carbonate being formed first. It is not known whether the nitrifying organism alone can attack organic matter and produce ammonia. It was at first stated by Mr. Warington that when nitrification takes place in a natural porous soil only nitrates are found, nitrites appearing only as products of reduction when air is excluded by an excess of water. This opinion, as will be shown, has had to be considerably modified. Nitrites are often formed in general, but are rapidly changed into nitrates in the presence of oxygen. Their production is favoured by the strength of the solution (this, of course, would only apply to surface drainage), by an alkaline reaction, by the presence of calcium or magnesium carbonate, and by a relatively high temperature. The natural tendency is for all the organic nitrogen to finally assume the form of nitrate. If plants, however, be present the nitrates formed are rapidly attacked and assimilated.

But if successive cultures are made in sterilised solutions of ammoniacal compounds, starting with a solution nitrified by soil, a point is soon reached when nitrites alone are produced, and these nitrites never change into nitrates. An alkaline condition of the solution is highly favourable to this change in the character of the process. Here the nitrites are not products of reduction.

The nitrifying organisms of Mr. P. F. Frankland and of Mr. Winogradsky only produce nitrites. Hence either the oxidation of ammonia to nitrites, and nitrites to nitrates, are distinct processes performed by different organisms, or else the original organism producing nitrate in the soil becomes weakened by cultivation and loses its faculty of turning nitrite into nitrate.

In special cases the complete oxidation of ammonia to nitrates (Mr. Munro) may be observed without formation of nitrite at any stage. This occurs in cases of extreme dilution, low temperature, presence of the nitrifying organism in considerale quantity, or in a very active condition, as in shallow layers of liquid freely exposed to the air. Sometimes the nitrite persists without alteration for months and then suddenly undergoes rapid conversion into nitrate.

This would probably be explained in the light of recent researches, by the accidental accession of another organism, or a fresh quantity of the same, the original organisms having been used up or enfeebled.

Bacteria, under different circumstances, produce nitrites (Messrs. Gayon and Dupetit), nitrogen oxides, and nitrogen gas. The whole of the nitrate may be reduced to nitrite without gas. They describe two organisms, *Bacterium denitrificans* A and B, of which the former is the more active in denitrifying, and also produces N_2O, whereas the latter liberates nitrogen only. They were obtained from sewage, but the mere exposure to unfiltered air of a liquid containing fermentible organic matter and a nitrate is almost certain to be followed in a day or two by the appearance of nitrite arising from reduction. The amount of nitrate destroyed is increased by diminishing the supply of air, and diminished when the air is ample.

These organisms, of course, account for the absence of nitrates and nitrites in sewage; both being finally pulled down to gas by the vigorously growing organisms.

When the whole of the nitrate is evolved as N, all its O combines with the carbon of the organic matter to form CO_2. The formation of N_2O is favoured by a comparatively high temperature, by a small quantity of the organism, and by the nature of the latter; thus, the A variety gives N and N_2O; B, only N. The denitrification requires the presence of organic matter to take up the oxygen. With a thorough circulation of air no denitrification occurs.

Messrs. Gayon and Dupetit supposed that there was a simultaneous oxidation of ammonia and reduction of nitrate, perhaps by this equation:—

$$NH_3+3KNO_3=HNO_2+3KNO_2+H_2O.$$

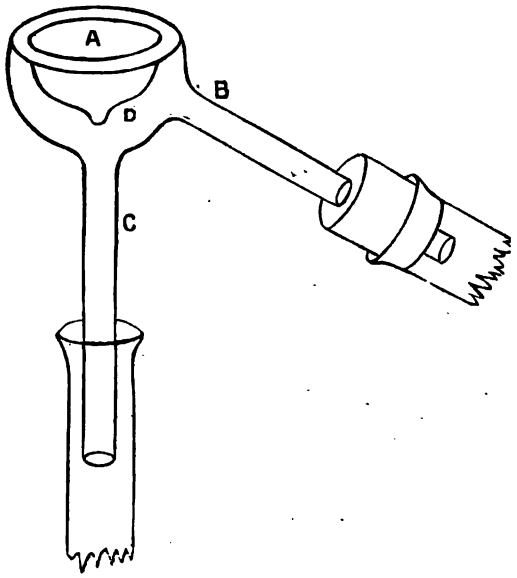
But Munro gives a table showing the gradual formation of nitrite from a solution containing NH_4Cl and KNO_3 with a little washed soil. The quantity of nitrate was approximately ascertained by the colour with metaphenylenediamine. It was found to increase for six months and then to decline, till in another six months it had disappeared. In most cases it persisted throughout the winter, but by the following spring had been completely converted into nitrate. He proves that at no time does the amount of nitrite exceed what is derived from the NH_4Cl (whereas if the above equation were true it might amount to four times the NH_4Cl), that the nitrate added was not reduced, that as much nitrite was formed when KNO_3 was absent as when it was present, and that the NH_3 was almost completely converted with nitrite before the commencement of the change into nitrate. Therefore the oxygen must be derived from the air, and not from the nitrate.

Bismuth Nitrosalicylates.—H. Caisse.—It results that even in dilute solution the nitric acid combined with bismuth acid transforms salicylic acid into β-nitrosalicylic acid capable of giving a series of salts the aspect of which varies with the composition.—*C. R.*, cxix., No. 17.

A TEST-TUBE CONDENSER.

By C. J. BROOKS.

THE accompanying sketch of a small condenser for use with test-tubes will be found useful for separating volatile substances on a small scale. The glass bulb, A, has a reservoir, D, in which the cooling medium is placed, on



the cold inner surface of which the vapour will condense as it is driven from the test-tube through tube B. The condensed liquid then falls through tube C, and is collected in another test-tube.

Chemical Laboratory,
King's College, London.

ON INDICATORS.*

By B. REINITZER.

(Continued from p. 226).

ALTHOUGH we have here exclusively to do with liquids containing carbonic acid, we cannot use methyl-orange, since the change of colour in this indicator, never very distinct, cannot be recognised at all by artificial light, whence its application in night-work becomes impossible.

It is common in alkali works to use methyl-orange for testing the finished soda, a kind of work which can be restricted to the hours of day-light. But here the advantage is not so great as it might be expected from the foregoing. Since methyl-orange is only available in cold liquids, the soda must be dissolved in cold water. Were we to use hot water and allow it to cool, we should lose the only advantage of the use of methyl orange, *i.e.*, the possibility of simpler and more expeditious work. Even the experienced operator cannot quite avoid the formation of hard lumps when sprinkling the weighed powder of soda into the solvent water in a porcelain capsule. These lumps dissolve very slowly in the acid as it is added, and have to be crushed in the liquid, whereby the accuracy, the speed, and the convenience of the test are affected. Further, the sharpness of the change of colour, which with methyl-orange is not all that could be desired, is diminished in consequence of the liquid to be titrated, which is here inevitable on account of the cold water of the solution.

It is a fact that with all the experience obtained from thousands of samples, the analyst is not able to titrate accurately to within 0·1 c.c. of acid consumed, and hence he cannot determine the proportion of soda more closely than to 0·2 per cent, which in a sample of sodium carbonate containing from 98 to 100 per cent, as it is at present guaranteed for ammonia-soda, is a serious consideration. Where strict accuracy is required, litmus and the ebullition process are still preferred, as we thus obtain results correct to the hundredths of a per cent. We may satisfy ourselves by a few experiments that methyl-orange is by no means more sensitive than litmus, but falls short of it both in sensitiveness and distinctness of the change of colour. The colour does not, as Prof. Lunge asserts, change suddenly and sharply from light yellow to purple-red, but passes from light yellow through a peculiar golden brown or dark yellow to a reddish yellow, such as in case of litmus is called onion red. This colour appears at once quite sharp and distinct if we have added to the liquid so much methyl-orange that on alkaline reaction it appears of a distinct golden yellow. If, as Prof. Lunge directs, we add to the liquid so little methyl-orange that it only appears visibly light yellow, the gradual change through brownish yellow to onion-red appears as above, but on account of the very faint colouration of the liquid it appears less striking to the unexperienced eye. This will be at once clear to everyone who, instead of normal acid, uses, say, decinormal acid, or who attempts to titrate a large volume of liquid, say, 0·5 to 1 litre. In order, in 250 c.c. of liquid, to pass from pure light yellow to a distinct onion-red, from 2 to 3 drops of normal acid are needed, and, of course, 20 to 30 drops of decinormal acid; that is, in other words, we are in the latter case so doubtful as to the conclusion of the reaction that, with such a volume of liquid, titration with deci, normal alkali is impossible.

The same case occurs with normal acid if the volume of liquid to be titrated is very large, about 1 litre. If we take smaller volumes of liquid, 100 c.c., as, *e.g.*, Thomson did in his comparative investigations, titration with methyl orange and decinormal acid becomes possible, but here we require 6 drops of decinormal hydrochloric acid, =0·19 c.c. for the transition, and lose in consequence almost entirely the advantage of using a decinormal acid. In these conditions Thomson consumes 0·5 c.c. decinormal sulphuric acid, or about 16 drops.

What are the conditions when using litmus? We keep 1 litre of distilled water in full ebullition in a flask of Jena apparatus-glass for eight to ten minutes and cool it then as far as possible in a strong stream of water. With this water, free from carbonic acid, we rinse out a few flasks and measure into each 250 c.c. of the same water and add a few drops of the litmus solution prepared as above directed, so as to produce a distinct—not pale—violet colouration. If the solution of litmus has been properly prepared, the violet is neutral, inclining neither to blue nor to red.

To one of the flasks we add a drop of decinormal hydrochloric acid. The colour turns at once to a vinous red. To a second flask we add a drop of decinormal alkali. The colour on shaking changes to a pure blue. If we allow both to stand for one minute, both the vinous red and the blue take a violet tint, but they can still be sharply distinguished. The red solution now requires exactly two drops, = 0·06 c.c., decinormal alkali to become blue, and the blue two drops of alkali to turn vinous red.

If we wish to effect the transit from a pure blue (which no longer reverts, and is free from the violet tint) to an equally permanent rose-colour, or inversely, 3 drops, = 0·09 c.c., decinormal liquid are needed.

A moderately experienced eye readily distinguishes the neutral pure violet from the blue and the vinous red so

* From the *Zeitschrift fur Angewandte Chemie*, September 15, 1894.

sharply that it can stop at this violet, and will therefore find a single drop sufficient for the transition.

If, instead of 250 c.c. of water, we take 500, the sensitiveness of the reaction is scarcely at all affected. Two drops of decinormal acid or alkali are still sufficient to occasion a sharp transition.

This great sensitiveness, however, exists only in cold liquids. It decreases in proportion as it is heated, and close upon 100° 5 drops, = 0·15 c.c., of a decinormal liquid are required to produce the same change of colour, from red to violet-blue, for which in the cold 2 drops, = 0·06 c.c., are sufficient.

If we test in the same manner phenolphthalein for its sensitiveness, we shall need for the same distinct change, from colourless to violet (not red !), in 250 c.c. cold water, 0·08 to 0·09 c.c.; that is, 3 drops decinormal alkali.

(To be continued.)

QUANTITATIVE ELECTROLYTIC ANALYSIS.*

By ALEX. CLASSEN.

(Concluded from p. 227).

Manganese.

ACCORDING to the experiments made in this laboratory, none of the methods hitherto in use are available for the quantitative determination of this mineral as peroxide. We assume that the peroxide dried at about 68° has the composition MnO_2+H_2O, a statement which I am not able to confirm. If we attempt to render the moist peroxide anhydrous by prolonged desiccation at a higher temperature, there results a strongly hygroscopic substance, which, on the balance, rapidly increases in weight. It is therefore necessary to convert the dry peroxide obtained into mangano-manganic oxide by ignition, a process which succeeds easily and certainly. After I had ascertained the conditions for the separation of large quantities of lead peroxide, I was led to assume that manganese must behave like lead. But experiments soon convinced me that strong mineral acids, such as the sulphuric and nitric, delay or altogether prevent the complete separation. Among organic acids, only the acetic was found suitable, but the deposition of larger quantities, even in matt capsules, is excluded, since firmly adhesive deposits cannot be obtained. As formerly reported, the deposition of lead in presence of nitric acid is practicable even if other metals are present. The hope that manganese in an acetic solution might be determined even in presence of iron was not fulfilled.

The proportions used were 0·5 grm.—

$$MnSO_4(NH_4)_2SO_4+6H_2O,$$

dissolved in about 75 c.c. of water with 25 c.c. of acetic acid (sp. gr. 1·069), the density of the current was 0·3 ampère, the tension at the electrodes was 4·4 to 4·9, the temperature 50° to 68°, the duration of the process three hours.

Separation of Lead from Copper.

The operation was conducted as described (*Berichte*, xxvii., p. 124). In the liquid decanted off from the lead peroxide, the copper was determined after the liquid had been rendered alkaline with ammonia, and then acidified with 5 c.c. of nitric acid.

Antimony from Arsenic.

With 1 grm. tartar emetic and 1 grm. sodium arseniate, the author used 80 c.c. solution of sodium sulphide (sp. gr. 1·13) and 2·5 grm. sodium hydroxide. The density of the currents was from 0·4 to 1·6, the tension was 1·75 to 1·1 at the conclusion, the temperature 21° to 57°, the duration from three and a half hours to over night.

Antimony from Tin.

Recent experiments have shown that for the deposition of antimony in presence of tin *in heat* the density of the current, $N.D_{100}$, = 1·5 ampère, so that the process may be completed in two hours. The deposits were free from tin.

Copper from Iron.

During the electrolysis a saturated solution of oxalic or tartaric acid was added from time to time.

Copper from Nickel.

To the mixed solution ammonium oxalate was added for the formation of the double salt. The electrolysis was effected in heat, and the liquid kept acid by additions of oxalic, tartaric, or dilute acetic acid. The tension at the electrodes must be kept within the limits of from 1·1 to 1·3 volt. The tension may be regulated by introducing the author's "sieve-resistance" into the circuit. (See Classen, "Quant Analysis by Electrolysis," ed. 3, p. 41).

Copper from Cobalt.

The same conditions must be observed as in separating copper from nickel.

Iron from Aluminium.

The solution employed was a double oxalate. To prevent the adhesion of aluminium hydroxide to the iron strong currents must be avoided.

Iron from Chromium.

The solution operated on was here a double ammonium oxalate. The initial currents had the densities of 2·0 to to 1·6 ampères; the tension, 3·2 to 3·8; temperature, 62° to 68°; duration of process, three to five hours.

Iron from Cobalt.

Both metals are precipitated from the solutions of the double oxalates. The sum of both is determined, and the iron is taken volumetrically.

Iron from Nickel.

The principle of the determination is the same as above. As the deposition of the last traces of nickel is tedious, the current used must be at least $ND_{100}=1$ amp.

ON THE

RELATION OF THE ATOMIC WEIGHTS OF HYDROGEN AND OXYGEN.

By LOTHAR MEYER and KARL SEUBERT.

JULIUS THOMSEN has recently published an account of experiments by which he determined the relation of the atomic weights of ammonia and hydrochloric acid. He obtained the mean value:—

$$NH_3 : HCl = r = 0{\cdot}467433,$$

i.e., a number less by 0·056 per cent than that deduced from the atomic weights as determined by Stas. According to the latter—

$$NH_3 : HCl = 17{\cdot}01 : 36{\cdot}37 = 0{\cdot}467693$$

(if H=1 and O=15·96; if H=1 and O=16, we obtain 0·467479).

From the very good agreement of the various experiments executed by Thomsen, we may infer, supposing that they contain no constant error common to all, that hitherto either the equivalent of ammonia has been assumed a little too high, or that of hydrochloric acid too low, whilst certainly the results of the accessible determinations of the atomic weights lead rather to the opposite supposition. Thus, Stas, on comparing ammonium chloride and silver, obtained the proportion—

$$NH_4 : HCl = 17{\cdot}03 : 36{\cdot}37 = 0{\cdot}4682,$$

which is higher by 0·2 per cent than that deduced from Thomsen's experiments.

Thomsen has now drawn from his experiments a further inference, since he used them for calculating the proportion of the atomic weight of oxygen and hydrogen, and arrived at the conclusion that—

$$H : O = 0{\cdot}99946 : 16;$$

or, within the limits of unavoidable error, 1 : 16.

This result must especially surprise us at present, now numerous recent determinations show for this proportion almost exclusively values which lie between 15·88 and 15·96, and therefore decidedly testify against the many-times contested view that the number 16·00 assumed, according to Prout's rule, gives accurately the true proportion of the two atomic weights.

A closer scrutiny gives rise to fundamental objections against the inferences drawn by Thomsen from his calculations.

In order to establish the proportion of the atomic weights O : H up to a unit of the second decimal (*i.e.*, the fourth figure), as it appears desirable, observations are required the errors in which do not extend to this place, and are therefore smaller than—

$$0{\cdot}01 : 15{\cdot}96 = 0{\cdot}06 : 100.$$

In other words, the possible error must not exceed one-half thousandth of the value to be determined. Thomsen's determinations do not satisfy this requirement, and indeed from grounds of the arithmetical order.

The method which he selects is indirect, and as such is open to the defect that all experimental errors appear in the result to a multiplied extent. In the present case the uncertainty (assuming the ascertained proportion, r, as free from errors) lies in the numerical value of Cl and N used in the calculation, as Thomsen himself explains. But he seems to us to form too low an estimate of the possible influence of this source of error in view of the great fundamental importance of the question to be decided.

Herr Thomsen calculates the atomic weight of hydrogen from the equation—

$$H = \frac{r\,Cl - N}{3 - r},$$

by introducing into it the ascertained value of r and the atomic weights of Cl and N referred to, O = 16·00. He thus obtains, assuming the atomic weights Cl = 35·457 and N = 14·041, for H a number which comes very close upon unity.

$$H = \frac{0{\cdot}467433 \cdot 35 \cdot 457 - 14{\cdot}041}{3 - 0{\cdot}467433} = \frac{16{\cdot}575 - 14{\cdot}041}{2{\cdot}532567} =$$

$$= \frac{2{\cdot}534}{2{\cdot}532567} = 1{\cdot}0005.$$

But the numerical values of the atomic weights of Cl and N are doubtful even in the fourth figure (the second decimal); consequently, in the numerator of the fraction (*i.e.*, in the remainder $r\,Cl - N$, the second decimal—that is, the third figure—is uncertain). An error of one unit in this figure occasions here (in view of the smallness of the remainder) one-half per cent of the value, whilst in order to decide in the affirmative the controversy whether the proportion of the atomic weights of O and H is a whole number, an accuracy of at least 1 to ¼ thousandth part is necessary. In one case O = 16·044, and in the other O = 15·954.

These numbers differ from each other by 0·06 per cent of their value, from which it follows that the proportion of the atomic weights O : H cannot be deduced with such a degree of certainty that they can be equally trustworthy with the direct determinations of this value.

The difficulties of a certain experimental determination of this question are certainly very great, since to obtain accuracy extending to the fourth figure 10 to 20 grms., or 110 to 220 litres, of hydrogen have to be weighed. Stas, as he informed one of us, considered about a plan for decomposing electrolytically an entire litre of water and separating the hydrogen on a very large kathode of platinum. But he never had the opportunity of carrying out this gigantic experiment. Perhaps the powerful electric forces so easily met with in great cities may aid the enquirers in its execution. Or the palladium method used by Keiser may, if carried out on the large scale, lead to the decision of this question of such great scientific importance.—*Berichte d. Deutsch. Chem. Gesell.*

ACTION OF LIGHT ON BACTERIA AND FUNGI.*

By Professor H. MARSHALL WARD, D.Sc., F.R.S., F.L.S.

(Continued from p. 230).

It is evident that the foregoing method is capable of application in several different directions, and I now proceed to attack the problem as to which rays of light are most effective in the process of destroying the living germs, on entirely new lines.

Starting from the thought that all the older attempts to compare the growth in two or more tubes exposed to different coloured lights are open to the criticism that it is impossible to be sure that each tube-culture is alike at the commencement, and extremely difficult to contrast them as growth proceeds, it was obviously a step forward to compare the effects of different coloured lights on one and the same plate-culture. This I did in various ways, but the following is one of the most instructive.

A block of vulcanite is cut in the shape of a Roman capital E lying on its back ⊔, and a thin glass plate is cemented to each side; this gives a double-celled screen, of which each cell is equal as regards depth of liquid poured in, kind of glass, and so on, points of more importance than may appear at first sight. Having prepared such a screen with, say, clear water in one cell and the orange-coloured solution of bichromate of potassium in the other, an agar plate of spores is made and *two* stencil letters placed on it, so arranged that one letter is covered by each cell of the screen.

[Screen apparatus of various kinds shown and explained].

On exposing such a screened plate, one, of course, gets the comparative effects of the *same* light, acting at the *same* temperature, for the *same* period, on the *same* culture; the one condition altered being that certain rays—in this case the blue-violet—are cut off by the bichromate screen.

[Plates thus exposed and photographs of such shown].

By thus using various coloured solutions, capable of cutting off certain rays of light—their behaviour in this respect being carefully determined by spectroscopic examination—in the one cell of the double screen, and water in the other, I was enabled to show very clearly the comparative action of the coloured light and the undecomposed light passing through water, and to establish the following conclusions.

There is no perceptible bactericidal action behind any screen which cuts off the *blue-violet rays*, whereas *the action is the more pronounced the more these rays are transmitted*. It matters not how much of the red-orange and yellow end of the spectrum is transmitted; so long as the blue-violet end is cut off by the screen, the spores are not killed at the ordinary temperatures. Results entirely confirmatory of these were also obtained with glass screens, although I now lay less stress on these, because they are in some respects less satisfactory for exact quantitative results, owing to the variations which glass screens show

* A Lecture delivered at the Royal Institution of Great Britain, April 27, 1894.

as regards their capacities for absorption and radiation.* [Photographs of exposures behind other screens].

Numerous experiments were also made, with screens and without, to test a number of other points of discussion which arose during the progress of the investigation —*e.g.*, how long an exposure was necessary to kill all the spores; how far temperature aids or combats the destructive effects of the blue rays; and so on. In these cases screens of quartz, alum, quinine, æsculin, rock-salt, and various other substances were used, and a number of interesting facts obtained as to details.

During the course of the enquiry as to the time necessary, it was found to be useful to photograph the plate after exposure in order to record the gradual process of "development of the image"—as the photographer would term it—as the spores on the non-illuminated parts of the agar film germinated out and grew into colonies, the opacity of which showed up the clear figure of the exposed area by contrast; and some suggestive facts were elucidated by these experiments.

On unwrapping the exposed plate nothing is visible at first, as already explained, but after twelve to twenty-four hours or so, at a suitable temperature in the dark, the spores on the non-illuminated parts of the plate gradually produce a faint grey opacity around the exposed area, which is so far a clear ill-defined patch. In the course of another twelve to twenty-four hours or so, the outlines of the letter or other shaped area begin to show more definitely, and the figure can be recognised, and later on it becomes sharper and sharper as the contrast between the more and more opaque and dense bacterial growth around, and the clear area containing the invisible dead —killed—spores becomes greater.

In certain cases, especially on very hot sunny days, when the light is particularly bright, it is found that the image is blurred for a long time, owing to the *retardation* (not death) of the spores in the immediate neighbourhood of the margins of the figure. The explanation of this phenomenon seems to be that the excessively intense light passing through the stencil letter and the transparent floor on which the spore-laden agar film rests, is partly reflected and slightly diffused from the surface of the glass lid of the Petri dish, and this reflected light is still strong enough to have some effect, and consequently the spores nearest the margins of the area through which the light comes are retarded, but not killed.

[Demonstration of the gradual development of the figure during incubation].

Another phenomenon of interest here is that a few spores here and there sometimes escape being killed, even on the most exposed parts of the illuminated area, and after a few days slowly grow out into feeble colonies. For some time this puzzled me considerably. It is clearly not evidence in support of any poison theory; but it seems very simple if we suppose these spores to have been so disposed that a number of other spores, vertically situated between them and the incident rays of light, sheltered them more or less completely—a disposition quite possible when we remember the millions of spores present in the film—and so saved them from complete destruction. And all the evidence points to this being the right explanation.

It only remains to be added here that all the effects already referred to can be got with the electric arc light, instead of with solar light, but there are some difficulties in employing this source of radiation, which may easily lead to the erroneous conclusion that the electric light is less efficacious as a bactericidal agent than sunlight. The principal of these is that, as we shall see, *glass in any form* is powerfully *obstructive to the rays required.*

It occurred to me at an early stage in this investigation—in fact, my earlier efforts were especially directed to this end—that the most direct answer to the question, What rays are the really effective ones? ought to be best obtainable by *shining the spectrum itself directly on the film of spores*, and making the latter *record the effects themselves*, by their subsequent behaviour, according as red, yellow, blue, &c., rays fell on them. For, obviously, if the spores are killed by blue-violet rays, and not injured by red and yellow ones, those spores which lay in the blue, &c., of the spectrum ought to die, and the agar remain clear, while those in the red, &c., ought to grow and render the agar opaque, and so on, and I ought to obtain a *photograph, in living and dead bacteria, of the spectrum itself!*

It is too long a story to go over all the difficulties and disappointments incident to the preliminary trials; but the ultimate success was so astoundingly complete and instructive that I must give some account of it.

The chief difficulty to be overcome here is the great weakening of intensity of the dispersed rays of the beam of light decomposed to form the spectrum; for not only are we here distributing the incidence of the rays themselves over a larger area, but they are passing through lenses, prisms, &c., which absorb or reflect many of them. This, of course, has to be compensated by condensing the beam and exposing for longer periods; but even then, when anything like a pure spectrum is employed, the slit has to be so narrow that relatively little light can be utilised. Consequently, the exposure has to be much more protracted than with undecomposed light.

Then came in another difficulty. It was found, when working with the electric light, that very feeble effects could be got as compared with those produced by exposure to the solar rays on a clear blue day, and the reason of this is that the blue and violet rays are stopped to a large extent by the glass surfaces through which the rays must pass. The effect of the glass is practically the same as the effect of mist or haze, &c., in the atmosphere, which so filters out the blue-violet rays that the light of a dull day is of little effect in my experiments.

During the progress of the experiments I had the good fortune to obtain the aid of Professor Oliver Lodge, who was so kind as to expose a large number of my plates to a powerful electric arc for me, with most satisfactory results. The difficulties referred to were got over by employing *quartz* instead of glass—the lenses and prisms were of quartz and a quartz plate was used for covering the agar film with its embedded spores.

In this manner it was possible to obtain a very pure spectrum sufficiently rich in blue and violet rays to kill the spores in a few hours.

With the solar rays I found it quite easy to obtain satisfactory results in the summer, however, even with glass mirrors, lenses, and prisms, and exposures of five to six hours, though in winter I find the exposures necessary are so long as to be almost impracticable.

I will first describe the experiments with the solar spectrum which I made at Cooper's Hill in the summer of 1893.

The plate of agar, with spores of bacilli in it, is made exactly as before, but instead of the ordinary glass lid I employ a sheet of thin flat ground glass, in which a slot is cut about three inches long by one inch wide. This slot is covered by either a thin sheet of glass or a plate of quartz. The whole of the covered plate—except the slot described—is then protected from the light by black paper and tin foil, and is then laid, bottom downwards, on a box kept cold with ice, in such a position that the spectrum falls vertically across the slot, the coloured bands crossing the long axis of the slot at right angles.

[Demonstration of quartz-covered plates and apparatus for spectrum and method of exposure, &c.]

The red rays are made to fall across, say, the left end of the slot, starting about half an inch from its extremity, then come the orange-yellow and green, then the blue and violet, the end of the visible violet being about an inch from the right end of the slot. Beyond the visible red, to the left, the invisible infra-red rays are falling on

* I am glad to take this opportunity of thanking Mr. G. W. Walker, of the Royal College of Science, for the trouble he has taken recently in physically testing a series of these glass screens for me.

the plate, and beyond the visible violet, to the right, fall the invisible ultra-violet rays.

Owing to the obstruction of the glass, however, very little of what ultra-violet escapes absorption in the atmosphere reaches the agar-plate itself; though, as we shall see, a good deal of the large proportion of these rays which emanate from the electric arc are incident on the plate provided no glass is employed at all.

The plate which I now have thrown on the screen [photographs of solar spectra in bacteria] was thus exposed for five hours in August to the spectrum obtained by decomposing a beam of solar light reflected from the mirror of a heliostat, and you see that the result is a most satisfactory proof (1) that the infra-red, red, orange, and yellow rays are totally without effect—as shown by the bacteria exposed to these rays having germinated and developed as rapidly and as strongly as those in the dark; (2) that the bactericidal effect occurs in the blue-violet region, diminishing in intensity at both ends as we pass into the green (to the left), or into the ultra-violet (to the right); (3) that the most destructive rays are the blue rays to the right and the violet rays.

These results are—if we allow for differences of absorption in the screens, &c.—entirely in accordance with my screen experiments, and prove most conclusively that *the rays which kill the bacteria are the blue and violet* ones. This explains why I find these organisms destroyed so much more rapidly by the light of the summer sun than in winter; why a clear blue sky is so much more effective than a hazy one; why direct sunlight acts so much more quickly than reflected or diffuse daylight; and many other experimental facts. It will be noticed that no question of temperature comes in; the plates are exposed on ice, and the hotter regions of the spectrum are totally without effect—the bactericidal action is here emphatically due to rays which affect our eyes as blue and violet. Now let us examine the results obtained with the electric spectrum.

The methods are exactly as before, excepting that the light, concentrated by quartz lenses, is passed through quartz prisms, &c., and is not allowed to pass through glass at all, unless, as in the case I will select, a piece of thin glass is interposed for experimental purposes, to determine the difference in effect between it and quartz. In this case two slots were cut in the glass lid, one of which was covered with thin glass, the other with quartz. Everything else was as before. The plate was exposed for twelve hours to a very pure spectrum, and it brings out very clearly the following facts. [Photographs of electric spectra shown.]

(1) That when there are plenty of ultra-violet rays, and no glass is interposed, the effect extends far beyond the visible spectrum into the ultra-violet, to the right; but when even a thin sheet of glass is interposed it obstructs these rays, and the effect is like that of the solar spectrum, as the photograph shows.

(2) It shows even more clearly than before that the infra-red, red, orange-yellow, and green are without effect, and that the effect weakens as we pass beyond the visible violet; and

(3) That the *maximum* bactericidal effect is due to the blue-violet rays, for the bellying out of the cleared region about there is due to the action of these rays reflected from the interior of the plate, showing that here alone are the reflected rays powerful enough to act just beyond the edges of the area.

It is also worth notice how slight an obstacle suffices to cut off the ultra-violet rays, for the two small protuberences visible in the lower photograph are merely due to two little drops of the Canada balsam used for cementing the quartz to the glass having oozed out and overflowed beyond the edge of the slot—nevertheless, this sufficed to block out the rays there.

These experiments will suffice to convince you that the blue-violet end of the spectrum is the effective one. They compel to the conclusion that the more I can expose the spores, &c., to the unobstructed rays, the more rapidly are the germs destroyed, and they show very clearly how fallacious may be the results where glass has to be employed throughout—a fact which will be impressed yet more upon us as I proceed.

There is another thought which arises here, and that is, what a poor chance such germs as these spores of fungi, yeasts, bacteria, &c., must have if they were not shrouded from the solar rays by the atmosphere! This reflection is not without its significance towards certain wild hypotheses as to the origin of life on our planet.

A more practical outcome of these results with the electric arc suggests itself in the probable efficiency of the naked arc light as a disinfecting agent in hospital wards, railway and other carriages, &c., as I have pointed out elsewhere; and we cannot overlook their significance in connection with such experiments as those of the late Sir William Siemens on the application of the electric light in horticulture, &c.

If now we look at these extremely suggestive experimental results from another point of view, it is obvious that these incubated plates showing the contrast effects between dead and living bacteria, or bacteria partly killed, as the case may be, and according as they have been exposed to light or not, or exposed to certain rays, or to others, or exposed for longer or shorter times, and so on, are really *photographs;* but they are photographs where the sensitive agent is a living organism, such as a bacterium, in place of a merely chemical substance, such as a silver salt suspended in a medium which acts as a carrier—here gelatin or agar, in place of the prepared gelatin of the photographer.

The plates I have shown you are really *photographs in living bacteria* of the solar and electric spectra, only instead of being recorded by the various stages of decomposition of the invisible particles of silver salts, which are then treated by chemical solutions, &c., in the processes of development, fixing, &c., they are recorded by the various capacities for germination of the invisible spores, the image—*i.e.*, contrast effect—being then *developed by my favouring their germination and further growth into opaque colonies* by the application of slight heat.

If this is so, it ought to be possible to use such a film of bacteria spores as a sensitive plate for printing from a negative, according to the principles laid down, and just as a piece of paper or glass, covered with a film impregnated with silver salts, &c., is used in contact printing in photography; and this, too, I have succeeded in doing. The chief difficulty to be overcome here is to bring the film impregnated with bacteria sufficiently close to the gelatin surface of the negative to be printed from, for of course it is impossible to bring them in actual contact, since the bacterial film must be kept covered by sterilised glass, &c., and the bacterial culture kept safe from contamination by spores in the air. By employing sheets of extremely thin glass, such as that used for cover-slips, however, on which to support the bacterial films, I have overcome this difficulty, and now throw on the screen a *photograph in living bacteria of a piece of English landscape*, printed from an ordinary negative by throwing the solar rays, reflected from a polished mirror of speculum metal, through the negative, the gelatin surface of which was only separated from the bacterial film by such an extremely thin plate of glass as I have described.

The bacterium employed was a beautiful purple one obtained from the Thames, and which is very sensitive to light—so much so, indeed, that I am convinced that with thin quartz plates I could get a print in half an hour on a clear day. In the case shown the exposure was only two hours.

It only remains to add that similar results with stencil-letters, the solar and electric spectra, and photographs such as that described have been obtained with anthrax, typhoid, several ordinary river bacteria, and fungi and yeasts, and that—apart from details which need not

enter into discussion here—the general results are the same.

(To be continued).

PROCEEDINGS OF SOCIETIES.

UNIVERSITY COLLEGE, LONDON, CHEMICAL AND PHYSICAL SOCIETY.

October 31st, 1894.

"*Sulphonation of Oils.*" By S. G. HALL.

When sulphuric acid reacts with an oil, an evolution of heat takes place which varies according to the oil that is being used. It was suggested that useful information as to the nature of the oil, and, to some extent, in the case of mixtures, as to the amounts of the constituents, might be obtained.

In making an examination, it was found that 25 grms. of oil and 5 grms. of 97 per cent acid were convenient amounts to take. These were placed in a glass cylinder and shaken vigorously for a few seconds; the maximum temperature reached was then compared with that obtained with the same amount of acid and 25 grms. of water.

Thus 25 grms. of water and 5 grms. of acid produce a rise of temperature of 38·6° C.; 25 grms. of olive oil and 5 grms. acid produce a rise of 35·3° C.

This method of comparison is called the specific temperature reaction. It is absolutely necessary to use identically the same apparatus in the two determinations, so that a comparison may be made under the same conditions.

The following results have been obtained by different experimenters—among them Maumené, Aleyne, Baynes, and Archbutt:—

Menhaden	125°	Poppy	72°
Cod oil..	110	Beechnut	65
Linseed	103	Rape oil	58
Seal	92	Olive oil	42
Whale	90	Lard oil	41
Cotton seed.. ..	75	Oleic acid	38

The following results were obtained with acids of different strengths, comparing the results as obtained by the Maumené and S. T. R. methods:—

	95·4		96·8		98·0	
	M.	S.T.R.	M.	S.T.R.	M.	S.T.R.
Water ..	38·6	100	41·4	100	46·8	100
Olive oil..	35·3	95·5	38·5	94	44·3	95
Rape oil..	49·0	127	—	—	58·0	125
Castor oil	34·0	88	37	89	—	—
Linseed ..	104·8	270	—	—	125·2	269

Oils that give large rises of temperature are diluted with a known quantity of olive oil.

Some oils, chiefly "drying oils," give very varying results. Thus rape oil gave readings between 125° and 144°; cod oil between 243° and 272°; and linseed oil between 270° and 340°.

Royal Institution.—The Christmas Course of Lectures, adapted to children, at the Royal Institution, will be delivered by Prof. J. A. Fleming, F.R.S., Professor of Electrical Engineering in University College, London. The subject will be "The Work of an Electric Current," and the first Lecture will be delivered on Thursday, December 27th, at three o'clock.

NOTICES OF BOOKS.

A Treatise on Chemistry. By Sir H. E. ROSCOE, F.R.S., and C. SCHORLEMMER, F.R.S. Volume I., the Non-metallic Elements. New Edition, completely Revised by Sir H. E. ROSCOE, assisted by Drs. H. G. COLMAN and A. HARDEN. With 374 Illustrations and a Portrait of Dalton, engraved by C. H. Jeens. 8vo., pp. 888. London and New York: Macmillan and Co. 1894.

THE *magnum opus* of Roscoe and Schorlemmer, in its earlier editions, has been generally pronounced a most admirable specimen of a complete work on chemistry. Not, indeed, that every fact in the vast compass of the Science is here put on record, or that every proposed generalisation is discussed. But all that is really essential and fundamental is fairly brought forward, and for details we are referred, in the abundant biographical notes, to original memoirs, or to works of a more special character. The present edition we are convinced will be found even more satisfactory than its predecessors.

In the historical introduction (pp. 3 to 40) we find the author speaking, if anything, too favourably of the phlogistian doctrines and its upholders.

In a section on the general principles of the Science (pp. 41 to 125), the author recognises provisionally the arbitrary classification of the elements as metals and non-metals, but he promises to explain the periodic system in a subsequent volume. On the capital question of the character of our present accepted elements he considers that we may, "with a considerable degree of probability," assume that they will yet be decomposed. The properties of gases are explained, with the laws of Boyle and Dalton; the kinetic theory of gases; the continuity of the gaseous and liquid states of aggregation; the liquefaction of gases; the laws of chemical combination, by weight and by volume; the methods of determining molecular weights; and, lastly, the principles of chemical nomenclature.

The author then takes up the non-metallic bodies *seriatim*, from hydrogen to silicon, arsenic ranking next to phosphorus as a member of the nitrogen group.

It will be perceived that Sir H. E. Roscoe does not confine himself in this work to the experiments of the laboratory. He includes also industrial operations. Thus the manufacture of sulphuric and nitric acids, of ammonia, phosphorus, coal-gas, &c., are described, with the aid of many well-drawn illustrations.

We are glad to find that the honour of the discovery and introduction of coal-gas as a general illuminant is ascribed to William Murdoch, followed up by Drs. Henry and Clogg. The pushing energetic attempts of Winzer (or, as he called himself, Windsor) to claim the discovery are passed over in charitable silence.

In speaking of water-gas, its composition, and the dangers and escapes of a mixture so rich in carbon monoxide, might have been more fully pointed out.

Under arsenic, the precautions necessary for the detection of this poison in toxicological cases, and in examining wall-papers, muslins, &c., are fairly described, though reference is made to special works, in which every step of the process is more fully described. It is not reassuring to learn that the "Styrian vice" has spread to Britain and to the United States. We have been shown, in a penny journal, no fewer than four different advertisements, all recommending arsenical preparations as cosmetics. Surely the Pharmaceutical Society might usefully turn its attention to the sale of such products.

On the subject of ozone and its quantitative determination the author speaks with judicious reserve.

Hydrogen peroxide is noticed as occurring in the atmosphere, and as being perhaps confounded with ozone. For its determination the colorimetric determination of Schöne is recommended.

The dangers involved in the use of phosphorus in the

match trade are not overlooked; but we may ask whether it is not possible to confine this substance to its legitimate use, the food of plants?

Under Fluorine we find a diagram of the apparatus used by Moissan in isolating this formidable element.

Concerning drinking-waters the author considers that the chemical examination of a water is a much more rapid process, but yields even less direct information as to the wholesomeness of the sample than the bacteriological.

The chemical world will eagerly wait the appearance of the succeeding volumes of this admirable work.

The Rise and Development of Organic Chemistry. By Carl Schorlemmer, LL.D., F.R.S., late Professor of Organic Chemistry in the Owens College, Manchester, Victoria University. Revised Edition. Edited by Arthur Smithells, B.Sc., Professor of Chemistry in the Yorkshire College, Leeds, Victoria University. Small 8vo., pp. 280. London and New York: Macmillan and Co. 1894.

A second and revised edition of this interesting and valuable work will be eagerly greeted, not merely by his former pupils and friends, but by all who are aware of the excellent service which he rendered to the study of chemistry in Britain. Premature as we must call his death, the work he did in Manchester is fructifying. We are very glad to learn that the chair of Organic Chemistry in Owens College will not be merged, and that a laboratory for the especial study of that department of the Science, due to the liberality of his admirers, is rapidly approaching completion, and will prove a noble monument to his memory.

The work before us, though it is immeasurably removed from the flimsy superficial manuals which have been of late so common, will, we believe, not be pronounced dry and unreadable even by outsiders of culture and intelligence. Schorlemmer here teaches organic chemistry biographically and historically. The reader is caused to stand, as it were, at the cradle of organic chemistry, to see it entering upon an independent existence, and passing through a series of controversies which might be likened to the diseases of childhood.

In the biographical notice of the author we find it remarked that he, at Owens College, "was exposed to the attractions of applied chemistry; and in a community which had the discernment to employ men like Mond, Caro, Martius, and Pauli, these attractions may have been considerable." Most true; at the same time we must regret that the community had not the discernment to train up such men in its own midst. To effect this it would be merely necessary to get rid of Examinationism. But, despite the logic of facts, we cling to it "like a torpid bat to a dead bough."

In the author's account of the origin of chemistry, he says, very aptly, that as Mechanics is the science of masses, and Physics that of molecules, so Chemistry is the science of atoms. He points out that historians have been in error in denying to the ancients in general the love of observation and experiment. They would, however, doubtless have had more and abler observers had it not been for the influence of Socrates and his school, which has not unjustly been called the "great apostacy."

The errors of alchemy, of phlogistic chemistry, and the beginnings of quantitative chemistry, are clearly depicted. So likewise is the influence of Wöhler's great discovery leading to the renunciation of vitalism as a special force on chemistry.

Succeeding chapters expound the doctrine of organic radicles; the theory of substitution, opposed as it was by Berzelius, but which is now beginning to find its application in some departments of biology; the nucleus theory; the theory of types; the reconciliation of the radicle and type theories; and the beginnings of the theory of valency.

In Chapter V. it is shown that compound radicles exist in inorganic compounds as well as in organic substances, and that consequently organic chemistry cannot be correctly called the study of compound radicles. The opposition of Kolbe to the structural formulæ of Kekulé and others, and to the stereo-chemistry of van 't Hoff and Lobel, are described, not without humour. The diagrams of "indigo *à la* umbrella and indigo *à la* tower steps" are exceedingly comical.

Schorlemmer's views as to the future triumphs of synthetic chemistry are exceedingly sanguine. Morphine and quinine may some day be obtained artificially, but it by no means follows that such success would be conveniently remunerative. Nor are we at all certain that it would be desirable, at least to us Britons.

The book before us is enriched with a portrait of the author, and a bibliography of his published researches. We feel confident that it will be widely read, and that, as did his lectures, it will re-kindle the zeal of every true student.

CORRESPONDENCE.

ESTIMATION OF CARBONATE AND CAUSTIC ALKALIS IN MIXTURES.

To the Editor of the Chemical News.

Sir,—From Mr. Aslanoglou's letter (Chemical News, vol. lxx., p. 232) in reply to Mr. Wilson, it appears that he is still unenlightened as to the cause of the enormous errors in his analysis of mixtures of carbonates and caustic alkalis by phenolphthalein. It would really be ludicrous, if it did dot excite impatience, to find Mr. Aslanoglou announcing as a discovery that phenolphthalein is alkaline to carbonates, and that it ought to be neutral if the method is correct. There exists no method founded on the supposed neutrality of phenolphthalein to carbonates, except in the mind of Mr. Aslanoglou. The merest tyro knows that carbonates are alkaline to phenolphthalein, but bicarbonates neutral.

I venture to draw the attention of Mr. Aslanoglou to the Chem. News, vol. lxx., p. 187, where he will find the cause of his error explained, and his experiment repeated under proper conditions. I should hardly have thought it worth correcting, except for the sweeping condemnation of phenolphthalein and as illustrating the danger of the careless use of indicators. There is no *universal* indicator, and the best of them may appear worthless if improperly used.—I am, &c.,

C. A. Seyler.

Technical Institute, Swansea.

Mr. H. Joshua Phillips, F.I.C., F.C.S., late of the Great Western and Great Eastern Railways, has opened practice as an analyst and consulting railway chemist, at Palace Chambers, Westminster Bridge, London.

The Comma Bacillus in Relation to Cholera (*Journ. de Pharmacie et de Chimie*). — According to M. Grimbert the most certainly Asiatic comma bacillus cannot occasion cholera, unless it finds in the organism an especially favourable medium. A factor still unknwn must therefore intervene, perhaps another microbe the association of which with the comma bacillus is necessary to occasion the disease. But until this hypothesis is verified we are forced to recognise that Koch's comma bacillus has lost a part of its importance, since it may circulate in the waters without bringing the cholera, and may swarm in the intestinal canal of man without occasioning choleraic symptoms.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxix., No. 17, October 22, 1894.

Experimental Researches on the Congelation-point of the Different Mixtures of Alcohol and Water.—Raoul Pictet.—The author gives his results in the form of a diagrammatic curve and of a table.

A Study of the Combinations of Hydrofluoric Anhydride with Water.—R. Metzner.—The author concludes from the totality of his researches that, in the conditions of his experiments, hydrofluoric acid forms only a hydrate with one mol. of water, $HFl.H_2O$.

Researches on the Mercuric Sulphate.—Raoul Vernet.—A thermo-chemical paper. The author has determined the formation-heat of mercury sulphate. The action of water upon this salt is that which evolves the greatest possible quantity of heat. This explains why this salt is decomposed by water into free acid and a basic salt, an exothermic reaction, whilst it would be endothermic with alkaline or metallic salts which are not decomposed by water.

Antimonial Vermilion is not an Oxysulphide.—In cold or in heat, with "emetic" and tartaric acid, the colouring matter of antimonial vermilion formed by sodium thiosulphate, *in as far as it is a chemical species*, is the ordinary sulphide, Sb_2S_3. There is no formation of oxysulphide in this reaction as Wagner has pretended.

Revue Universelle des Mines et de la Metallurgie. Vol. xxvii., No. 3.

Total Desulphurisation of Liquid Cast-Iron by Barium: its Alloys and its Haloid Salts.—A. de Vathaire.—The author has solved the problem by the use of the non-oxidised salts of barium, especially the ferrocyanides, which are easily decomposed by heat into iron, carbon, and barium. Barium ferrocyanide is obtained by mixing the concentrated and boiling solutions of yellow prussiate and of barium chloride. A double barium and potassium ferrocyanide obtained by mixing equivalent weights of the two salts in solution has generally given the best results. The reaction must be effected in the exclusion of air and of every oxidising action. On melting in a lined crucible with the cover luted, a mixture of the sulphurous cast metal and of barium prussiate, with the addition of fluor-spar, it is easily perceived that all the sulphur passes into the slag around the ingot.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. ix., No. 104.

This issue contains no chemical matter.

MEETINGS FOR THE WEEK.

TUESDAY, 20th.—Institute of Civil Engineers, 8.
WEDNESDAY, 21st.—Society of Arts, 8. Opening Address of 141st Session, by Major-General Sir John Donnelly, K.C.B.
—— Institution of Mining and Metallurgy, 8. "The Practical Operation of the Cyanide Process on the Witwatersrand (Transvaal) Goldfieldr," by Manuel Eissler.
—— Meteorological, 7.30.
—— Geological, 8.
—— Microscopical, 8.
THURSDAY, 22nd.—Royal, 4.30.
—— Institute of Electrical Engineers, 8.
FRIDAY, 23rd.—Physical 5. "The Measurement of Electromagnetic Capacity," by Frederick Womack. "On Mirrors of Magnetism," by Prof. S. P. Thompson and Miles Walker. "Students' Simple Apparatus," by Prof. Ayrton and others.

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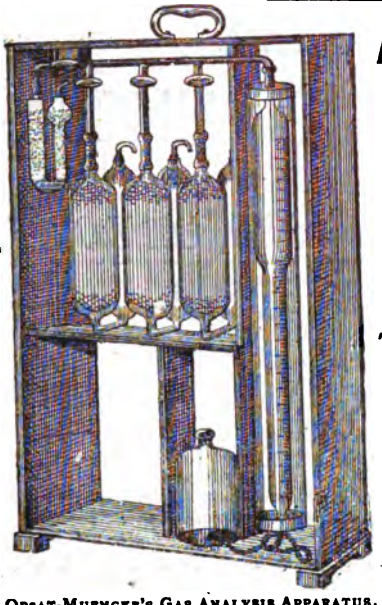

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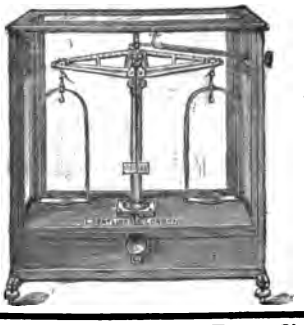

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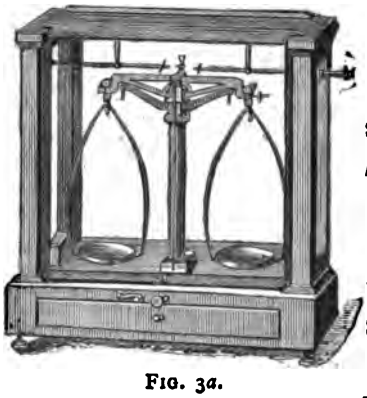

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THE CHEMICAL NEWS.

Vol. LXX., No. 1826.

RECTIFICATION OF THE ATOMIC WEIGHT OF CARBON.

By J. ALFRED WANKLYN.

The December number of last year's *Phil. Mag.* closes with the following paragraph, contributed by myself:—

"An investigation which has occupied me for the greater part of the year has yielded the following remarkable result:—There is a series of hydrocarbons the successive members of which rise in molecular weight, not by $CH_2=14$, but by $\frac{1}{2}CH_2=7$. If this result cannot be overturned the consequence follows that the atomic weight of carbon is 6."

The series was published in the Chemical News of January 19 of the present year, and those of your readers who will turn to the issue of that date will find that fourteen successive terms are shown where the increment is 7 instead of 14.

Since that time the subject has been further investigated, and in the May number of the *Phil. Mag.* there is a paper by Cooper and myself on "Fractional Distillation Illustrated by the Investigation of Kerosene," and, as your readers will know, the Chemical News of Aug. 24, 1894, reports my paper on this subject, which was read at the Oxford Meeting of the British Association.

The result arrived at by Cooper and myself is that Russian kerosene (which has been known for many years as a complex mixture of hydrocarbons with the same percentage composition as olefiant gas) consists of a series of hydrocarbons which rise by increments of 7 instead of 14. As we remarked in our paper in the May number of the *Phil. Mag.*, the lower terms of the series are present in very small proportions in commercial kerosene, and we have had to operate on a considerable scale in order to obtain sufficient material for satisfactory examination. We have distilled more than 200 litres of kerosene, and from that quantity of the raw product have obtained from 150 c.c. to 200 c.c. of the hydrocarbon labelled A*x*, and about 75 c.c. of A*y*, and about 30 c.c. of A*x*.

The liquid A*x*, formula C_7H_{14}, requiring a vapour density 3·386, has given a vapour density 3·43. It has a constant boiling-point, which, using one of Casella's standard thermometers, was found to be 85° C. at 760 m.m. pressure. The specific gravity of the liquid at 15·5° C. is 0·746.

The next liquid, A*y*, formula $C_{6\frac{1}{2}}H_{13}$, vapour density 3·144, was found to have a vapour density 3·192. It boils constantly at 74° C. Specific gravity of the liquid 0·735 at 15·5° C.

The 30 c.c. of liquid labelled A*x* has been examined and found to be considerably mixed; that is to say, it consists of more than C_6H_{12} and $C_{6\frac{1}{2}}H_{13}$. Apparently there is at least one liquid of smaller molecular weight than 84. The quantity of material is much too small to admit of a satisfactory separation, and we hope to be in a position to obtain a sufficient supply in the near future.

Up to the present time we have isolated the successive terms of a series of hydrocarbons, beginning with a molecular weight of 91 and boiling point of about 74° C., and ending with a molecular weight of 196 and boiling-point of about 222° C. Of these sixteen terms every molecular weight, except one, has been established by determining the vapour density.

Inasmuch as the inevitable result of this work is at variance with the prevalent views of chemists at the present moment, I was not surprised that the validity of fractional distillation as a means of separating volatile liquids should be denied. But I do not expect that the denial will be persisted in, for the validity of fractional distillation has been established by countless experiments, and in fact there is hardly any chemical research in which volatile liquids are dealt with which does not in some way involve the validity of fractional distillation. My own experience of fractional distillation dates back nearly forty years. During the years 1855, 1856, and 1857, in the humble capacity of private assistant to Dr. Frankland, I was initiated into the mysteries of fractionation, and my experience teaches me that a mixture of a series of stable hydrocarbons is exactly such a mixture as falls within the scope of the method. Tedious and laborious the work may be, but the result is sure.

HYGROSCOPIC MOISTURE IN NITRO-CELLULOSES.

By CLAYTON BEADLE.

During the preparation of a number of nitro-celluloses of varying yields from cotton-wool I was struck by the relationship that appeared to exist between the amount of nitrogen present and the gain of weight when the anhydrous nitro-cellulose was exposed to the atmosphere. I thereupon prepared nitro-celluloses in three series, and weighed each sample before and after taking up atmospheric moisture. The yields are expressed in the following series, on the supposition that cellulose equals 100:—

	Yield.	Moisture.
(1) to (8).—		
(6).	162·8	1·84 per cent.
(7).	158·1	1·65 ,,
(8).	147·3	2·11 ,,
(3).	139·5	3·44 ,,
(5).	140·1	3·93 ,,
(2).	135·1	4·43 ,,
(1).	131·5	4·41 ,,
(4).	129·6	5·54 ,,
(11) to (17).—		
(17).	142·2	2·46 ,,
(12).	139·1	2·95 ,,
(11).	139·1	3·17 ,,
(13).	126·9	4·41 ,,
(15).	124·4	4·84 ,,
(16).	121·9	5·16 ,,
(14).	119·8	5·42 ,,
(18) to (26).—		
(23).	155·7	1·28 ,,
(18).	152·8	1·57 ,,
(24).	147·3	1·97 ,,
(22).	148·5	2·00 ,,
(19).	146·7	2·03 ,,
(21).	145·7	2·12 ,,
(26).	149·4	2·55 ,,
(20).	141·1	3·26 ,,
(25).	135·9	3·23 ,,

It will be noticed that the hygroscopic moisture varies inversely as the yield, and therefore directly as the OH groups left unsaturated. This affords further evidence that the hygroscopic moisture of cellulose is in some way a function of the OH groups (see also Beadle, *Journ. Franklin Inst.*, Aug., 1894). The three series cannot be compared with each other as the moistures were determined on different days. Differences of atmospheric conditions probably account for the difference between each series. Each member of a series may be compared, as they were weighed under similar atmospheric conditions. The hygroscopic moisture does not appear to be affected by the physical condition of the nitro-cellulose, nor by its

method of preparation or precipitation, as the following description will show.

Cellulose nitrates prepared from pure cellulose (cotton-wool) as follows :—

1. 1 grm. cotton-wool, air dry; 20 minutes in 20 c.c. fuming nitric, precipitated with water.
2. 1 grm. cotton-wool soaked in water and pressed until it weighed exactly 2 grms.; 20 minutes in 20 c.c. fuming acid, precipitated with water.
3. Exactly the same as 1.
4. 1 grm. cotton-wool containing 2 grms. of water after squeezing; time, acid, and precipitation the same as above.
5. 1 grm. cotton-wool dried at 110° C., otherwise the same as above.
6. The same as 4, but precipitated with sulphuric acid.
7. The same as 2, but precipitated with sulphuric acid.
8. The same as 1, but precipitated with sulphuric acid.

The following, from 11 to 17, are 1 grm. lots of cotton-wool dissolved in 20 c.c. fuming acid; 2½ hours at 60° F., and precipitated with water 30 c.c.

11. Air dry.
12. Air dry.
13. Weighing exactly 2 grms. after squeezing.
14. Weighing exactly 2 grms. after squeezing.
15. Weighing exactly 3 grms. after squeezing.
16. Weighing exactly 3 grms. after squeezing.
17. Dried at 110° C.

The following 18 to 24 the same in order as the above 11 to 17, but precipitated with 20 c.c. sulphuric acid instead of water. Time in fuming acid 1 hour.

25. The same as 24.
26. Bone dry cotton-wool treated in the mixed acids, resulting from 25 after precipitation.

NOTE ON LOSS OF HEAT BY IMPERFECT COMBUSTION.

By W. A. DIXON, F.I.C., F.C.S., Tech. Coll., Sydney, S.W.

Tatlock, in the Chemical News (vol. lxx., p. 51), on the "Heating-power of Smoke," shows that the amount of heat which is lost, through the incomplete combustion of coal, in the form of unconsumed carbon, is so small as to be practically negligible. He, like most others, assumes that the loss of heat is due entirely to this unconsumed carbon, which is not the case. Tested by the calorimeter, fairly good coal shows an evaporative power of about 13 lbs. of water for 1 lb. of coal on an average, whilst in actual working the effect is seldom more than 8 lbs., and often less, so that there are 5 or more lbs. to be accounted for. This is partly used for the production of chimney draft, and partly lost in radiation, and it is evident that all heat passing into the chimney beyond that necessary for draft is wasted.

The production of smoke promotes this waste in two ways; first, by depositing a non-conducting coating of soot on the boiler and tubes; and second, by the suspended smoke not acting as a screen to the radiant heat from the fire, so that the escaping gases are unduly heated. It is well known to engineers that the steam raised from the radiant fuel in the fire-box, or from flame, gives the greater portion of the effect in a boiler, and any screen would of course diminish this. That smoke acts as such a screen I have often noticed when, being in sunshine, a cloud of smoke from a steamboat funnel has passed, so as to form a cloud, when you immediately feel the effect of the shade. I have also found, experimentally, that the temperature of a reverberatory furnace is much increased by admitting air, so that smoke disappears, whilst the flame is kept a reducing one.

The analyses of furnace gases given by Tatlock show that three times the necessary quantity of air was passing through the furnace; but even if the necessary quantity only was used, the rise in the temperature of the gases caused by the smoke preventing the passage of the heat into the boiler would cause great loss.

QUANTITATIVE DETERMINATION OF NICKEL BY MEANS OF AMMONIACAL MERCURIC CYANIDE.

By F. W. SCHMIDT.

As it was intimated in a former page on this subject (*Berichte*, 24, p. 2836), the determinations with ammoniacal mercuric cyanide can be transferred to other metallic sulphides. As the determinations of nickel present a general interest, I may presume to indicate briefly a quantitative transformation of nickel sulphide into nickel oxide.

For the determinations it was before all things necessary to find a convenient and practically easy method for the quantitative precipitation of nickel sulphide. Setting out from the fact that nickel sulphide can be completely separated by colourless ammonium hydrosulphate, and that the separation is promoted by means of ammonium salts, a few preliminary experiments led to the following process :—

The solution of a nickel salt plentifully mixed with ammonium nitrate is treated in a small Erlenmeyer flask with exactly so much ammonia as to give the liquid a faintly bluish colour. An excess of sulphuretted hydrogen water was then added to the solution placed over an open fire, whereby after a brief ebullition all the nickel was separated in the form of a bulky precipitate, which is easily filtered, and the supernatant liquid became colourless. The solution is filtered whilst still boiling, and the precipitate washed with sulphuretted hydrogen water to which ammonium nitrate has been added. The filtration and washing must not be interrupted. To verify the method there was used a 1 per cent solution of nickel prepared by dissolving 1 grm. of nickel (purified by an especial method which will be described in future) in nitric acid, and making up the solution to 100 c.c. Of this solution 10 c.c. were evaporated down and caused to smoulder (I.). Then from 10 c.c. of this solution the nickel was precipitated in the manner above directed in the state of nickel sulphide, the latter being converted into nickelous oxide by evaporation with ammoniacal mercuric cyanide and smouldering (II.).

The author states in a note that the evaporation is best effected on an iron plate heated by the small flames of the heating-worm of a gas-stove. The dried mass is heated at first cautiously, the edges of the crucible being heated by a circular motion of the Bunsen flame until vapours cease to escape. By degrees the entire side of the crucible (placed in a slanting position) is heated, and lastly the crucible is placed upright and heated with the full flame, and lastly ignited with the blast until the weight is constant.

The determination of nickel in this manner is free from difficulty.

The following observations may elucidate the action of ammonium nitrate in the precipitation of metallic sulphides :—I first observed a decomposition of the solutions occasioned by neutral salts on a close examination of the white zinc sulphide, soluble in ammonium carbonate. If to a solution of this substance in ammonia we add calcium chloride, magnesium sulphate, and other neutral salts, it is separated out apparently unchanged. The yellow solution of oxysulpharsenious acid, formed by mixing an aqueous solution of arsenic trioxide with sulphuretted hydrogen water, behaves in a similar manner. From this solution arsenic trioxide is precipitated by sodium chloride, potassium iodide (quantitatively !), am-

monium carbonate, magnesium carbonate, &c., whilst formerly it was known only that such a solution is precipitated by the addition of hydrochloric acid. The fine orange-red solution of sulph- or oxysulph-antimonious acid (hitherto unknown), which I obtained by mixing a strongly diluted solution of tartar emetic with sulphuretted hydrogen water, is decomposed by the addition of certain neutral salts. All these solutions hence behave like solutions of colloidal bodies, which gives a simple explanation of the fact that the presence of neutral salts promotes the separation of sulphides. It may easily be shown in like manner that a solution of nickel sulphide in ammonium sulphide is quickly decomposed by ammonium nitrate even in the cold, but rapidly if heated, provided that it does not contain an excess of ammonia.

Finally, it may be mentioned that the conjecture that "ammoniacal mercuric cyanide is transformed on evaporation with certain natural sulphides, *e.g.*, copper pyrites, in an analogous manner," is fully confirmed. Not only the greenish iridescent powder of finely pulverised copper pyrites turns black on evaporation with ammoniacal mercuric cyanide, but the residue of the evaporation dissolves completely after ignition and subsequent evaporation with hydrochloric acid. The operation described can be effected in a short time, whilst the customary method for the oxidation of copper pyrites with fuming hydrochloric acid (?) or potassium chlorate and hydrochloric acid requires several days.—*Berichte*, No. 12, p. 1624.

ON INDICATORS.*

By B. REINITZER.

(Concluded from p. 240).

If we use an equal volume of water near the point of ebullition about 10 drops of decinormal alkali are needed to effect the change of colour, which has then rather a rose shade.

If the pale violet-red liquid is allowed to cool it assumes visibly a deep red fiery colour. Hence phenolphthalein in the cold is about three times as sensitive as near 100°, and its behaviour in this respect is thus quite similar to that of litmus.

If we finally apply the same method of examination to methyl orange we consume in a cold liquid (250 c.c.) to effect a decided change from pale yellow to onion-red, 0·48 c.c. = 16 drops of decinormal hydrochloric acid. In a liquid heated to nearly 100° 0·2 c.c. of normal solution or 2·0 c.c. of decinormal solution are required for the same transition. Hence Lunge directs titration in the cold. This remarkable behaviour, hitherto nowhere mentioned, seems to hold good for all indicators, and may have its cause in a dissociation of the combination of the indicator with the alkali or the acid increasing progressively with the temperature, so that the excess of alkali or acid necessary for the production of a given change of colour in one and the same liquid increases with the temperature.

From these experiments it further results that litmus and phenolphthalein far exceed methyl orange in sensitiveness and —what cannot be sufficiently emphasized— also in the sharpness of the transition of colours, whence the two former indicators admit of use by gas-light. If in these the transitions are somewhat less distinct, it is still possible to work with decinormal solutions, whilst with methyl orange it is quite impracticable even with normal solutions. These results can scarcely surprise us on careful consideration. It is quite intelligible that colouring matters which are so sensitive as litmus and phenolphthalein, not only to weak organic acids, but even to carbonic acid, must in general be more sensitive than methyl orange, which is almost inert to the above acids and even to oxalic acid. The opposite case would be scarcely comprehensible.

The above considerations are not intended to throw doubt on the utility of methyl orange in volumetric analysis. But it must take its right place in the series of indicators, and must not be allowed to displace others, not because they are apparently "hallowed by time," but because of their high advantages.

* From the *Zeitschrift fur Angewandte Chemie*, September 15, 1894.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING OCTOBER 31ST, 1894.

By WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, November 10th, 1894.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 189 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from October 1st to October 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 189 samples examined, seven were recorded as "clear but dull," the remainder being clear, bright, and well filtered.

The rainfall during the month of October, at Oxford, representing the Thames Valley, has been 3·97 inches, and as the 25-years' mean for the month is 2·56 inches, it follows that there has been an excess of rain amounting to 1·41 inch. Most of the rain fell at the latter part of the month, no less than 3·27 inches falling on five days, the 24th, 26th, 27th, 28th, and 30th, the rest of the month only having 0·7 inch of rain. The effect of so much sudden downpour is to wash a certain amount of clay into the river from the adjacent country, and thus introduce suspended matter into the water. So far the filtering arrangements of the respective Companies have been well able to cope with the additional strain thereby put upon them, as may be seen by the clearness of the waters as recorded in Table II.

It will be noticed that the Grand Junction water, at the beginning of the month, was not perfectly clear. Some of the filter-beds at the Hampton works are in course of partial reconstruction, causing a disturbance of the filtering medium. We have therefore temporarily discontinued drawing samples from the Uxbridge Road for analysis, and have taken them from a stand-pipe in Kensington Park Road. Analysis shows that the turbidity is not caused by excessive organic impurity, but by purely inorganic and harmless matter. The efficiency of filtration, as regards the security of the public against any possibility of water pollution, is proved by the bacteriological examinations of the waters, which have been carried on during the last month; these show that the Grand Junction waters, as well as those of the other Companies, were practically free from microbes. In the least clear sample

of water drawn direct from the stand-pipe at Shepherd's Bush into a sterilised tube, there were detected only twenty colonies per cubic centimetre after cultivation for forty-eight hours in nutritive gelatin.

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

ON THE

CONSTITUTION OF THE ELECTRIC ARC.

By L. THOMAS.

The production of interference fringes with the light of the arc shows that a region near the negative pole is plainly monochromatic. If we simultaneously illuminate one-half of the field with the arc, and the other with a flame charged with sodium, we find that the two series of fringes agree exactly. The phenomenon is therefore due to the great brightness which the sodium-vapour acquires near the negative pole, relatively to the other gases present. We further recognise that it is on setting out from the negative pole that the vapour expands itself in the exterior flame.

There is room to suppose that this accumulation at the negative pole is not peculiar to sodium, but for the other substances the question can only be treated by means of the spectroscope. Now the modifications undergone by the metallic rays in different parts of the arc will be, according to Lockyer, most irregular, a substance showing at the same time certain rays near the positive pole, others near the negative pole, and others only in the intermediate region.

I have taken up this study having regard to the two following points:—

1. A modification in one ray cannot be certainly referred to a particular region of the source (of light) unless the image of such source, being projected on the plane of the slit, yields in the spectroscope for each point of the slit a linear spectrum; that is to say, we must realise the aplanetic regulation indicated by Cornu in his beautiful memoir on the groups A, B, a, of the solar spectrum, and which completes so usefully the method of Lockyer.

2. To escape the frequent modification of the arc it is convenient to reduce the observations to the shortest possible duration, and to this end it is sufficient to photograph the region of the maximum of sensitiveness of the plates.

The carbons employed are either ordinary carbons, the impurities in which are especially compounds of iron and calcium, or carbons with a core formed of a mixture of charcoal powder and a metallic salt. The latter, if the mixture is thorough and the proportion of the salt not too considerable, allow us to obtain very constant spectra.

The following are the facts observed:—

I. *Slit parallel to the Carbons, dividing the Arc into two equal parts.*

The metallic lines, visible over all the height, increase he lustre and the breadth from the positive to the negative: this increase is abruptly exaggerated in the neighbourhood of the latter; the lines which occupy only a part of the height extend to the negative; the inversion, when it occurs, is most marked near the negative; lastly, whilst some lines only extend over the interval of the carbons with little lustre, almost all traverse the negative and are extinguished only at some distance.

II. *Slit parallel to the Carbons, outside the Brilliant Circle which terminates the Negative.*

The spectrum is divided into two parts, situate at different levels: resting upon the positive carbon the spectrum of Swan, and the spectrum of cyanogen, and beyond the spectrum of the metallic vapours, presenting its maximum lustre near the level, where the lines of the first terminate in fine points.

III. *Slit perpendicular to the Carbons.*

The metallic rays extend much further than the lines of the band spectrum. The latter have the form of a breadth constantly decreasing from the middle to the ends, whatever may be the position of the slit between the two carbons. The metallic lines have the same form near the negative. Everywhere else they have a constant breadth except the points of the extremities.

Hence it is easy to understand the frequent changes observed from moment to moment on a direct examination of the spectrum, and the reason of the irregularities pointed out by Lockyer, and of some peculiarities which it would be too tedious to describe here.

Lastly, we see outside the arc, and principally near the negative pole, spectra of metallic oxides; the bands of calcium and barium are especially brilliant.

The totality of the facts is thus interpreted:—The arc formed of a mean length between two carbons containing metallic salts consists of a core and a covering. In the core are found the substances which give off band spectra, carbides or vapours of carbides, and cyanogen; in the covering, the metallic vapours derived from dissociated salts circulate from the positive to the negative carbon. The metallic molecules, after this electrolytic transportation to the negative pole, combine with the oxygen of the air and escape in the flame.

I have succeeded in obtaining a photograph of this stratum by placing before the object-lens a trough filled with fluorescein. The division is distinctly marked, in consequence of the partial solarisation of the proofs; the stratum alone is black; the core and the two brilliant surfaces which terminate the carbons are solarised. An interesting point is that the stratum cuts the negative carbon perpendicularly to the direction of the carbon, which is favourable to the spectroscopic study of the velocity of the mols. at the extremity of their track. This part of the covering presents deviations in the metallic lines, but, at least with the dispersions which I have been able to employ, these deviations are annulled at the same time as the astigmatism of the spectroscope.

From the above we may explain the differences of lustre and form of the two poles. Although no experiment proves the afflux of the elements of the air to the positive pole (except perhaps the presence of cyanogen in the core), it is nevertheless very probable, and must employ an important part in the elevation of the temperature of this pole. The arc will thus be a sort of gas voltameter. The positive carbon will be attacked by the gases brought up by the current, whilst the negative carbon will be protected from the access of air by the metallic vapours.

In support of this view I will cite the following facts:—

In a very rarefied atmosphere the sections of the arc near the two poles are sensibly equal; in hydrogen, under a pressure of about 10 c.m., we find a greater lustre of $H\alpha$ $H\beta$ near the negative pole.

In coal-gas, in an hour, the arc deposits upon the positive carbon a considerable and regular deposit of very compact carbon; the negative carbon shows a great number of craters.

If the positive carbon is covered with strontium chloride, the arc is stable only when the negative carbon is cut into a cylinder of small dimensions, rounded at the end, and the lateral surface of which the layer of strontium vapour is normally placed.—*Comptes Rendus*, cxix., p. 728.

Campholenic Acids and the Campholenamides.—A. Béhal.—We have now before us at least three campholenic acids, the amides of which melt respectively at 83°, 92°, and 127°.—*Comptes Rendus*, cxix., No. 19.

ACTION OF LIGHT ON BACTERIA AND FUNGI.*

By Professor H. MARSHALL WARD, D.Sc., F.R.S., F.L.S.

(Continued from p. 244).

In order to try and obtain a further insight into the physiological and pathological phenomena concerned in this bactericidal action of light, however, and in view of various disadvantages inseparable from the employment of cultures in the mass, I have attempted with success to trace the effects of the light on the *individual bacterium cell* itself, isolated under the microscope. To do this, some form of culture chamber is necessary in which the organism can be grown in a minute drop of food-material—such as broth, gelatin, or even water—and can be kept under a high power of the microscope for some hours, or even days if necessary. This is managed as follows:—

[Demonstration of culture cells and methods of using them.]

A glass tube, about 3 inches long, has a bulge in the middle; this bulge is ground down on two opposite sides so that it is pierced by two large round openings. One of these openings is placed downwards on a piece of glass or quartz, and cemented to the latter by any convenient means—I usually employ paraffin: the other opening, above, is covered by a thin piece of glass, to the underside of which, in the centre, is hung a minute drop of the food-material containing the spore to be examined. The two arms of this culture chamber are stuffed with wet cotton-wool, and a layer of water is placed on the floor of this "damp chamber," and the whole is now ready for use. All the materials employed have undergone the necessary cleaning and sterilising, and with proper precautions there is no reason why such a hanging drop, with the growing organism in it, should not be kept under observation until the latter has either exhausted all the food supplies, or completed its life-cycle, in focus under the microscope.

When in position on the stage of the microscope, the light reaches the organism through the glass or quartz, and of course it is easy to arrange shutters, screens, &c., so that only the light reflected from the mirror of the microscope below shall reach the drop and the organism in it. Again, it is easy to interpose coloured or other screens of glass, coloured solutions, &c., and so allow only certain rays to reach the hanging drop.

Now suppose a single spore in the drop to be placed in focus under the microscope, and that in the eye-piece of the latter a graduated scale is fixed, the value of whose divisions is known. In a few hours the spore, the length of which is measured, begins to germinate, and developes into a rod—a bacillus—the length of which is then measured; then measurements of the increasing length of the growing rod are taken at successive intervals, as convenient, and so ideas of the rate of growth of the rod obtained. If I sketch the elongating rod at appropriate intervals on sectional paper, to scale, always starting each sketch from the same horizontal base line, and at a distance along this line proportional to the time which has elapsed since the preceding sketch was made, the line joining the free ends of the rods gives a curve, which will be steeper or the reverse according to the rapidity of growth of the rod. Considerable use can be made of this *curve of growth of the bacillus.*

[Demonstration of the measurement of growth of the bacillus.]

Obviously it is easy to record these measurements by plotting them out in the form of a curve—the intervals of time being measured along a base line, and vertical lines (ordinates) in each case proportional to the length of the growing rod at the time, being erected at these points, and the joined upper ends of these ordinates give the curve.

[Photograph of a curve of growth of a bacillus.]

Now, I find that the curve of growth thus obtained is remarkably constant in shape under constant conditions of temperature, illumination, &c., but vary if these conditions vary. By comparing a number of such curves, moreover, much curious information is coming to hand, but as this does not concern our present theme, I shall not dwell on it here.

The steepness of the curve—*i.e.*, the rate of growth of the rods—increases with the age and length of the latter, when the conditions of growth are constant, because, as the rod increases in age and length, it exposes a larger and larger surface of absorption to the food-materials, and possesses more and more power of utilising them for further growth.

If two cultures such as those described are started at the same time, one under one microscope and the other under another by its side; and if *one* condition at a time is varied for one of these cultures, then the differences in the curves ought to give us a very clear idea of the effect of the difference of condition on the growth of the bacillus—and we must remember that the rate of growth is our best criterion for the well- or ill-doing of the organism.

It is, however, by no means an easy matter to vary *one* condition at a time in these cultures, and the principal difficulty of the whole of this more recent part of the research has been the attainment of this object as near as possible.

The most prominent and annoying form in which this difficulty has presented itself has been the following:—If I allow the sun's rays to be reflected up from the mirror into the culture-cell, in order to brightly illuminate the growing bacillus, the heat rays at the red end of the spectrum become effective in raising the temperature of the culture; whereas the culture on the other microscope, protected from the light, is also sheltered from these heat rays, and consequently the two cultures are not simply differing by *one* condition—it is not true that the one is growing merely in the dark and the other merely in the light, but the one is growing in the light *at a higher temperature* than the other.

This and similar difficulties had to be overcome, and it was clear that some means must be devised for recording the temperature *inside* the culture cell, and this I accomplished by placing a very small delicate thermometer, with its bulb blackened, *inside the culture cell itself*, so that each time when the register of the length of the bacillus was taken, the temperature of the culture itself was also recorded.

[Photograph and description of the control culture cells.]

By these means I have now succeeded in comparing the effect of light of even low intensity by direct observations of the bacillus itself, under high powers of the microscope, and in comparing the curves of growth under various conditions of light and of temperature, and this, moreover, on a Thames bacillus which is among the least sensitive of those which have yet come under my notice.

Since the details of this investigation have not yet been published, however, I must content myself with a few references only.

Just to illustrate how strikingly different the curves of growth in darkness and in the light may be, however, I now throw on the screen the curves obtained by measuring at intervals the growth of two cultures of this bacillus, one under a microscope fully exposed to the light, and the other under similar conditions, but in the dark.

[Photograph of curves shown.]

The temperatures recorded by the thermometers are given also; but I do not intend to go into this matter here, as I have a large number of records bearing on the matter—which is, moreover, an extremely complex one.

* A Lecture delivered at the Royal Institution of Great Britain, April 27, 1894.

I wish you to understand, however, that the enormous difference between these two curves is principally due to the differences in illumination, and that, as you see, the bacillus in the light took as long to grow 200 units of length as that in the dark did to grow 560 of the same units—in other words, the light *retards* the growth even of the actively vegetating bacillus, a fact quite in accordance with what we know of the growth of other plants. Moreover, I find the curves of growth differ when the bacilli are examined growing behind coloured screens, and in just the same way as we should expect from the foregoing.

The curves now shown were obtained by measuring the [Photograph of curves of growth in red and blue light.] growth of two cultures in the light, one behind a blue glass, the other behind a red one, and alum screens were employed to diminish the heating effect. Here, where bright sunlight was used, it took the bacillus in blue light the same time to grow 50 units of length that the one in red light required to grow over 1200 units.

And a large number of similar experiments all agree in pointing to the same end—the light acts as a retarding agent on the growth of the vegetative bacillus, as well as injuriously on the germinating power of the spores. In both cases it is the blue-violet rays which are effective, and if these rays are sufficiently intense, or act for a sufficiently long period, they kill the organism in the manner we have already seen.

Undoubtedly the most interesting results have been some of those obtained with light of relatively low intensity, acting on the spores themselves. First let me show you the curves of growth of three cultures of a bacillus from the Thames which I have been studying for some time, in which the spores had been dried by placing them at 80° C. in a hot oven, and allowing the temperature to fall slowly—it took two hours to cool to 30° C., as the best proof I can give you that these roasting hot temperatures do not injure the life of the spore, and that the results to be described are in no way due to temperature.

[Curves of growth of spores dried at high temperatures].

As the curves show, these spores germinate as rapidly and well as if merely ripened at the ordinary temperature and at once sown.

I may also add that the spores of the bacillus I am showing you will endure the broth or water, in which they are suspended, being raised to boiling-point for a minute, and may be kept at 55° to 60° C., and even higher temperatures, for many hours without apparent damage, though they do not survive prolonged boiling. Here is sufficient evidence, however, to prove that we are not dealing with spores which are at all tender to high temperatures, but with forms which are wholly unscathed by any such temperatures as they have to endure on exposure to the sunlight.

Yet an exposure of half an hour or so to the direct rays of the sun kills these spores outright.

But direct sunlight is not necessary, as the following experiment shows:—Four culture cells were prepared as described, each hanging drop having a small number (about 15 to 25) of spores in it, and placed each with a thermometer control cell as follows:—One was under a darkened bell jar; a second under a large flat-bottomed glass dish filled with clear water; a third under a similar dish filled with deep blue ammoniacal solution of cupric oxide; and the fourth under a similar dish of deep orange-coloured solution of potassium bichromate. [Demonstration of methods of exposure.] The first, therefore, was excluded altogether from the light, while the second received all the light passing through water and clear glass. The third was exposed to the feeble light passing through the very deep-coloured copper solution, and from which all red and yellow rays were cut off; while the fourth was exposed to the red and yellow rays only, all the blue-violet being excluded by the screen.

Now mark the conditions of exposure, as recorded on the chart. They were all outside, at the north, and in the shade of a building, so that no direct sunlight reached them at all—only the lights from the blue sky and clouds; moreover the temperature was low, and so nearly the same in each culture cell as that of the surrounding air, that even the most sceptical critic would not ascribe the results to the minute differences, even if we did not know from the other evidence that he would be wrong in doing so.

These cultures were exposed for five hours as described, and then all brought into the laboratory and placed in the dark at the same temperature—21° C.—a temperature chosen as being the most favourable for their further development. After a sufficient interval of time, the lengths of all the germinated bacilli in the drops were measured, and the means and averages taken, and plotted on sectional paper, with the results now shown.

[Curves of average growth of these thrown on screen.]

The results were that the spores which had been excluded from the light and those which had been sheltered behind the bichromate from all blue-violet rays, germinated out normally, and the bacilli rapidly developed and grew; those exposed to the blue rays (though of feeble intensity) were so far retarded that the curve of growth is markedly depressed; while those exposed to the more intense light coming through the clear water, and therefore to more intense light containing more of the blue and violet, were killed altogether, for they refused to germinate in all cases, and even after several days' nursing.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Extra Meeting, June 28th, 1894.

Dr. Armstrong, President, in the Chair.

This meeting was held in the Theatre of the Royal Institution, by kind permission of the Managers.

The following paper was read and experimentally illustrated:—

*44. "*Phosphorescence and Photographic Action at the Temperature of Boiling Liquid Air.*" By James Dewar, F.R.S.

Phosphorescence and fluorescence are terms applied to similar phenomena which apparently differ only in degree, the first lasting for a relatively long period after the withdrawal of the light stimulus, whereas the second is so short that it can only be observed during the continuous action of the exciting agent. In all cases the luminous effects called phosphorescence and fluorescence belong to a less refrangible part of the spectrum than the exciting rays. Phosphorescence may be regarded as a kind of fluorescence which lasts a long time after the excitation has ceased, and may be briefly defined as the phenomena observed when certain substances give out light through the transformation of absorbed vibrations of shorter period. The researches of Becquerel showed that the intensity of phosphorescence depended directly on the intensity of the stimulating light, and a factor of absorption and intensity as some coefficient representing molecular friction or damping. When phosphorescing sulphides of calcium are heated they increase in this light emission, whereas if cooled to −80° they cease altogether to be luminous, and if maintained at this low temperature for hours keep a latent store of light energy that may be again evolved on allowing the temperature of the sulphide to rise to the ordinary temperature. But while the temperature of −80° is sufficient to stop all sensible emission from previously excited sulphide, it does not prevent an

unexcited sulphide from *absorbing* light energy that can be evolved at higher temperatures. Having now the means of cooling substances to temperatures ranging from −180° to −200° by means of liquid air, a new study of phosphorescence seemed admissible. Under such conditions all known organic compounds are solids, and this condition of matter is specially favourable to phosphorescent phenomena.

The effect of temperature on phosphorescence is easy to observe by taking two portions of the same substance placed in similar very thin test-tubes, cooling one of the specimens in liquid air, and then quickly exposing both samples side by side to the same light stimulation. If during the light excitation, caused by burning magnesium or a flash of the electric light, the eyes are carefully covered, then the comparative phosphorescence, if any, of the cooled and uncooled substance can be observed. In this mode of working the action of the very short wavelengths of light are stopped by the opacity of glass, but the solid condition of all substances at the low temperature enables the use of glass to be abandoned when necessary. As a general rule it may be stated that the great majority of substances exhibiting feeble phosphorescence at ordinary temperature become markedly more active at these very low temperatures. Thus gelatin, celluloid, paraffin, ivory, horn, and indiarubber become distinctly luminous, with a bluish or greenish phosphorescence, after cooling to −180° and being stimulated by the electric light. Hydroquinone was more luminous than the isomeric resorcinol or pyrocatechol, and in the same way pyrogallol was faint compared with phloroglucol. All alkaloids forming fluorescent solutions become phosphorescent at low temperatures. The hydrocarbons, alcohols, acids, and ethers of the fatty series are all more or less active, and glycerin, sulphuric, and nitric acids are all very bright, so also are concentrated hydrochloric acid and strong ammonia solution. Coloured salts generally show little activity, but a large number of colourless salts are very luminous. Water when pure is only feebly phosphorescent, but remarkably so whem impure. Acetic acid and acetamide appeared fairly equal in luminosity; hippuric acid was very fine, as were most substances containing a ketone group. Lithium platinocyanide changed from white to red on cooling, and was excelled in phosphorescing power by yellow ammonium platinocyanide, which was exceedingly bright.

Definite organic substances possessing exceptional powers of phosphorescence when stimulated at −180° C. are acetophenone, benzophenone, asparagin, hippuric acid, phthalic anhydride, urea, creatine, urethane, succinimide, triphenyl methane, diphenyl, salicylic acid, glycogen, aldehyd-ammonia, &c. It will require long and laborious experiments, however, to measure the relative brightness of the phosphorescence of bodies belonging to definite series.

Remarkable results were obtained with an egg shell and a feather respectively. The egg shone brilliantly as a globe of blue light, and the feather was equally brilliant, its outline showing clearly in the darkened room. Other organic substances giving good results were cotton-wool, paper, leather, linen, tortoise-shell, and sponge, all phosphorescing brightly, as did also a white flower, a cultivated species of *Dianthus*. Coloured glasses and papers as a rule exhibit no phosphorescence, and when the alcohols are coloured by the addition of a trace of iodine the luminous effect is destroyed. Milk was shown to be highly phosphorescent and much brighter than water. The white of egg has greater phosphorescing power than the yolk, white substances generally being superior in this respect to coloured ones. On cooling a layer of white of egg on the outside of a test-tube to −190°, and then exposing it to a flash of the electric arc, the brilliancy of the phosphorescent light is very striking. The chloro-, bromo-, iodo-, sulpho-, and nitro-compounds, as a rule, show nothing, or are but faintly luminous. Amongst basic bodies, nicotine is more luminous than quinoline or pyridine. Metals also phosphoresce, but in this case the action is due to some organic film deposited from the air, because it disappears on ignition. If the metal is subsequently touched, the phosphorescence re-appears.

So far as the examination has been carried, the two most remarkable classes of substance for phosphorescence are the platinocyanides amongst inorganic compounds, and the ketonic compounds, like acetophenone and ethyl phenyl ketone, and others of the same type amongst organic. When ammonium platinocyanide is cooled with liquid air and maintained at this temperature by being immersed in the liquid while stimulated by exposure to a beam of the electric arc, it continues to glow in the dark with a feeble emission as long as the temperature is kept about −180°. On pouring off, however, the liquid air from the crystals so that the temperature may rise, then the interior of the test-tube glows like a lamp from the sudden increase of light emissivity as the temperature rises. It seems clear from this experiment that similar initial light intensities being used for stimulating, the substance at this low temperature must have acquired increased power of absorption, and it may be that at the same time the factor of molecular friction or damping may have diminished. That the absorptive power of substances for light is greatly changed at low temperatures is proved by the change of colour in substances like oxide, iodide, and sulphide of mercury, chromic acid, &c., when cooled. Many quantitative photometric measurements must be made before the actual changes taking place in the conditions governing the phenomena can be definitely stated.

Along with these experiments on phosphorescence, a number of photographs have been taken at −180°, using various sensitive plates and films, and these have been compared with similar photographs taken at the same time under similar conditions at the ordinary temperature. The photographs have been examined by Captain Abney, who reports that the photographic action has been reduced by 80 per cent at the temperature of −180°. If the photographic action is brought about by a chemical change, then it appears to be the only one that can be traced under such conditions, as substances having the most powerful affinities have no action on each other, and all voltaic combinations cease to give a current at such low temperatures. It is certain that the Eastman film cooled to −200° by the evaporation of air *in vacuo* is still fairly sensitive to photographic action. Much further work, however, will be required to reach a definite conclusion as to what is taking place when substances sensitive to photographic action are subjected to such conditions of temperature.

The following are the abstracts of papers received during the vacation, and published in the *Transactions*:—

45. "*The Magnetic Rotation of Compounds supposed to contain Acetyl, or to be of Ketonic Origin.*" Part II. By W. H. PERKIN, Ph.D., F.R.S. (*Trans.*, 1894, 815).

The following substances were examined as to their magnetic rotation:—Dimethylacetylacetone allylacetylacetone, hydracetylacetone, ethylic monocarboxyethylacetoacetate, ethylic-β-ethoxycrotonate, methylic acetoacetate, methylic dimethyl acetoacetate, ethylic dimethylacetoacetate, ethylic diethylacetoacetate, acetylacetone, and acetic anhydride; while allylacetylacetone, hydracetylacetone, and ethylic ethoxycrotonate were examined as to their refractive and dispersive power. Details of the results are given in the paper. The author finds that dimethylacetylacetone behaves only as a ketone, and concludes that the values given in his previous paper (*Trans.*, 1892, 800) for monomethyl and monoethyl-acetylacetone are a little too high. Allylacetylacetone is found to consist, at ordinary temperatures of the unsaturated hydroxylic compound; at 95° it principally consists of the ketone. Acetylacetone is the unsaturated monhydroxylic compound,—

$$CH_3{\cdot}C(OH){:}CH{\cdot}CO{\cdot}CH_3,$$

and hydracetylacetone is the saturated compound,—

$$CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CO{\cdot}CH_3.$$

Ethylic monocarboxyethylacetoacetate and ethylic-β-ethoxycrotonate are unsaturated compounds. The remaining substances show similar results to those previously obtained.

46. "*Studies on Citrazinic Acid.*" Part III. By W. J. SELL, M.A., and T. H. EASTERFIELD, M.A., Ph.D. (*Trans.*, 1894, 828).

On further examination of the product of the action of dilute sulphuric acid on isonitrosocitrazinic acid (*Trans.*, 1893, 1047), the authors regard it as αα-diglutaric acid. They have also prepared and described αα'-diglutaric acid, anhydrodiglutaric acid, and examined the products of the nitration and sulphonation of citrazinic acid.

47. "*Azo-compounds of the Ortho-series.*" Part III. By RAPHAEL MELDOLA, F.R.S., and EDGAR S. HANES. (*Trans.*, 1894, 834).

A description is given of the reduction of the acetyl-derivative of β-naphthaleneazo-β-naphthol with zinc dust and acetic acid, and of the preparation of α-naphthyleneazo-β-naphthol, metanitrobenzeneazo-paracresol, and of benzene-β-azo-α-naphthol. The methods of attack are summarised under the heads of reduction, nitration, and bromination. The first give ambiguous results in the case of azo-compounds containing acid radicles, but might be expected to give definite evidence of the constitution of alkyl derivatives; the second gives very decisive information in the case of alkyl derivatives of the azo-naphthols; the third has proved to be inapplicable to oxyazo-compounds.

48. "*Derivatives of Anthraquinone.*" Part III. By A. G. PERKIN and F. COPE. (*Trans.*, 1894, 842).

An examination of the properties of β-methylanthraquinone and of its derivatives. In the course of the inquiry the following substances were prepared and described:—*m*-hydroxyanthraquinone, β-carboxylic acid, alizarin-β-carboxylic acid, nitroalizarin-β-carboxylic acid, and purpurin-β-carboxylic acid. The latter product was compared with purpurin carboxylic acid or pseudopurpurin present in madder, and the distinction between the two was exceedingly well defined. The carboxyl group in these compounds is very stable.

49. "*Colouring and other Principles contained in Mang-Koudou.*" By A. G. PERKIN and J. J. HUMMEL. (*Trans.*, 1894, 851).

Mang-Koudou is the root bark of *Morinda umbellata*, largely used in Java for producing fast reds in the native calico prints. The authors correct their previous statement (*Trans.*, 1893, 1162), that its colouring matter was alizarin, and now show it to be morindone. They have isolated eleven distinct substances from the root, which also contains free acid, the nature of which has not yet been determined. No cane sugar was found, a distinction from chay root (*loc. cit.*) and from madder. Full details of the methods employed in extraction and separation are given, and the behaviour of the substance as a dye-stuff is described.

50. "*Phenylnaphthalenes.* II. *β-Phenylnaphthalene.*" By F. D. CHATTAWAY, B.A., and W. H. LEWIS, B.A. (*Trans.*, 1894, 869).

β-Phenylnaphthalene can be synthesised by allowing sodium to act at about 140° on a mixture of chlor- or bromobenzene and β-chlornaphthalene or β-bromonaphthalene dissolved in zylene. The yield is poor, but the method shows the constitution of the hydrocarbon. The product, distilling between 300—380°, consists chiefly of β-phenylnaphthalene. A yield of 2—3 per cent of the weight of β-chloronaphthalene used was obtained. Its properties are fully described. It melts at 101·5°, and boils at 345—6°. Its quinone was prepared, and is described.

51. "*Preparation of β-Chloronaphthalene.*" By F. D. CHATTAWAY, B.A., and W. H. LEWIS, B.A. (*Trans.*, 1894, 875).

β-Chloronaphthalene is best prepared from β-naphthylamine by diazotising it and converting the diazochloride into the chloro-derivative by means of cuprous chloride. As little water as possible should be present, and not more than 30 grms. of β-naphthylamine should be used. The final yield of the pure substance is about 75—80 per cent of the theoretical. The action of phosphorus pentachloride on β-naphthol yields only about 10 per cent.

52. "*Note on β-Mercurydinaphthyl and ββ-Dinaphthyl.*" By F. D. CHATTAWAY, B.A. (*Trans.*, 1894, 877).

β-Mercurydinaphthyl, prepared by Otto and Dreher's method, is examined and described. The author confirms Behren's results. When distilled over red-hot soda lime, it yields, among other products, ββ-dinaphthyl, which is also described. The author is engaged in investigating the dinaphthyls and their derivatives.

53. "*Reduction of Paratolueneazodimethylaniline.*" By D. R. BOYD, B.Sc. (*Trans.*, 1894, 879).

P. Jacobson and Kunz reduced benzeneazodimethylaniline with stannous chloride and hydrochloric acid, and isolated from the product a dimethyltriamidodiphenyl. As transformation into a semidine base was not observed, though the substituting group was in the para-position, it appeared possible that the action might take a different course if a substituted group were present in the second para-position also. This investigation has shown that paratolueneazodimethylaniline yields, on reduction, a semidine base in very considerable quantity. The paper gives an account of the method of preparing the paratoluene compound, its reduction, the isolation of the resulting base, its behaviour towards formic acid, benzil, nitrous acid, and its decomposition products when acted on with hydrochloric acid, which prove the base to be an ortho-semidine.

PHYSICAL SOCIETY.

Ordinary Meeting, November 9th, 1894.

Prof. A. W. RÜCKER, F.R.S., President, in the Chair.

THE meeting was held in the rooms of the Chemical Society, Burlington House.

Dr. J. LARMOR's paper on "*The Significance of Wiener's Localisation of the Photographic Action of Stationary Light-Waves*" was read by the Secretary, Mr. Elder.

The experiments by which Wiener demonstrated that, when stationary plane-polarised optical undulations are produced in a photographic film, by reflexion of a stream of plane-polarised light at a metallic or other backing, the photographic action occurs at the antinodes of Fresnel's vibration-vector and not at the nodes, have been employed by its author and others to decide between the various theories of light. Using the terminology of the electric theory of light, we may say that the photographic action takes place at the antinodes of the electric vector which corresponds to Fresnel's vibration, and not at the intermediate antinodes of the magnetic vector which corresponds to McCullagh's and to Neumann's vibration.

The crucial experiment of Wiener relates to the case when the angle of incidence is 45°, so that the direct and reflected waves which interfere are at right angles to each other. When the light was polarised in the plane of incidence, the photographic plate developed a series of bands; but when it was polarised in the perpendicular plane, these bands were absent.

The argument employed is that the photographic effect will be greatest at those places in the stationary wave-train where the vibration is most intense; and the conclusion has been drawn from it that the actual vibration is represented by Fresnel's vector, and not by McCullagh's; in other words, that the vibrations of polarised light are at right angles to the plane of polarisation. The force of this argument, as against McCullagh's theory, would,

however, be evaded if the vector of that theory were taken to represent something different from the linear displacement of the ether, or if vibrations were excited in the molecule by rotation instead of translation, or by stress.

Now there are about 10^8 molecules of the sensitive medium in the length of a single wave of light; thus in the stationary wave-train all the parts of a single molecule would at any instant be moving with a sensibly uniform velocity, which increases and diminishes periodically. It does not seem clear, however, that alternating stress might not be as potent a factor in disintegration as alternating motion.

The Author proceeds to discuss the question from the point of view of an elastic-solid-ether theory, and he points out (from dimensional considerations) that even a very rare medium of very low rigidity might powerfully influence the movements of foreign bodies suspended in it, provided the linear dimensions of such bodies were sufficiently small.

We may imagine a working illustration of a ponderable transparent medium of elastic-solid type, as made up of very small spherical nodules of great density and rigidity, dispersed through the ether and imbedded in it. A wave running across such a medium may excite these groups, thus illustrating selective absorption; the elasticity of the medium alone being operative, and no other internal forcive.

A theory based on difference of rigidity without difference of inertia, after McCullagh's manner, would have to be realised by ascribing to the atom an atmosphere of intrinsic ethereal strain instead of endowing it with great inertia; and this could only be possible in a rotational ether, and would in fact form a mechanical representation of the electric theory. As such it must be expected to give an account of the phenomena of electricity as well as of those of light, and in such an account is founded one of its chief claims.

The difference between the dielectric coefficients of a material medium and a vacuum is simply and naturally explained by the hypothesis that the material molecules are polar, owing to their associated atoms having equal and opposite charges. An electric force thus tends to pull the two constituents of a molecule asunder; and its full intensity is exerted in this manner, not merely its differential intensity over the range of the molecular volume. But a magnetic force would have no such tendency, even were the molecule magnetically polarised, because the two poles of a magnetic element cannot be dissociated. On the electric theory, therefore, there is abundant justification, both for the magnitude of the effect produced and for its localisation as determined by Wiener. The Author has endeavoured to show elsewhere that the principles of McCullagh's theory of optics are in substantial agreement with all the general features of our electrical and optical knowledge. It is definitively implied in the electromotive, as distinguished from an electrodynamic character of the electric theory of light, that the atomic charges vibrate in unison with the light-waves, quite unimpeded by any material inertia of their atoms.

A letter was read from Professor LODGE, criticising the manner in which Wiener's results had been summarised by Dr. Larmor, the summary at the commencement of the paper being characterised as misleading. The letter concluded with an expression of admiration for the work done by Dr. Larmor in working out electricity and optics, starting from McCullagh's theory of light.

Dr. STONEY objected to the suggestion that atomic charges could vibrate unimpeded by material inertia. We had not merely to consider the bodily translation of a molecule, but the relative motion of its parts. Radiation absorbed by a gas acted on its atomic charges; part appearing as translational energy of the molecules, part as energy of their internal motion, and the ether acting as an equaliser of molecular energy.

Prof. MINCHIN did not understand why the polarised light in Wiener's crucial experiment should be incident at 45°. He also found it hard to imagine what vector other than the simple displacement of the ether could be the vector of McCullagh's theory.

Dr. BURTON said he found no difficulty in following Dr. Larmor's statement of Wiener's results; it appeared to him perfectly clear and satisfactory.

Dr. SIDNEY YOUNG then read a paper on "*The Influence of the Relative Volumes of Liquid and Vapour on the Vapour-pressure of a Liquid at Constant Temperature.*"

The Author has very carefully examined the question raised by Prof. Battelli, whose researches have led him to the opinion that the vapour-pressure of a liquid at a given temperature depends on the relative volumes of liquid and vapour, being higher the greater the proportion of liquid. This conclusion is entirely opposed to the results obtained by Dr. Ramsay and the Author, the suggestion being that in Prof. Battelli's experiments an error arose from the presence of air or other impurity in the liquid examined, or in the employment of insufficiently purified substances for heating purposes.

In a letter published in the August number of the *Philosophical Magazine*, Prof. Battelli adheres to his conclusion, and does not admit the existence of either of the sources of error suggested. "I would rather observe," he writes, "that, in order to observe such a phenomenon, an apparatus is necessary which enables us—as in my case—slowly to compress the vapour, and to maintain it for a time under constant pressure." The Author thinks it hardly necessary to point out that these conditions are fulfilled in the apparatus employed by Dr. Ramsay and himself. During the present year he has been engaged in investigating the thermal properties of isopentane—a liquid boiling at 28°, which can, by suitable treatment, be obtained in a pure state. The results, it is claimed, prove conclusively that the vapour-pressures of isopentane are independent of the relative volumes of liquid and vapour. A table is given showing that (although the relative volumes of liquid and vapour vary between wide limits) there is no such corresponding variation in the vapour-pressures, the greatest difference from the mean value at 140° being slightly less than 0·1 per cent, and at 90° slightly greater—in no case outside the limit of experimental error.

The CHAIRMAN remarked that, although the *à priori* considerations against Prof. Battelli's view were very great, it was satisfactory to have had the experimental enquiry carried out with such care and accuracy by Dr. Young.

Mr. BURKE communicated a paper "*On a Suggestion of Professor J. J. Thomson in connection with the Luminescence of Glass due to Cathode Rays.*"

More than a hundred years ago Beccaria observed that when vacuum-bulbs were broken in the dark, a light consisting of a faint glow was produced in the place where the bulb lay. Beccaria was led by his experiments to attribute this effect to the rushing of air against the glass walls of the exhausted vessel; and in his "Recent Researches in Electricity and Magnetism" Prof. J. J. Thomson indicates its possible close relationship to Mr. Crookes's theory of the luminescence of the glass in Geissler's tubes. The Author, however, has made numerous experiments on the breaking of glow lamps, and on the admission of air to an exhausted chamber by the breaking of a thin plate of glass or of a piece of bladder closing an aperture in the walls. In these cases, and in other cases where it was possible for fragments of solid to be projected against the walls of the vessel, a luminous appearance was obtained; while in other cases, where such solid fragments would be absent, no luminosity was observed. The Author concludes that Beccaria's phenomenon was due to the impact of glass against glass, and not to the rush of air against the walls of the broken vessel.

ROYAL INSTITUTION OF GREAT BRITAIN.

General Monthly Meeting, Monday, November 5, 1894.

SIR JAMES CRICHTON BROWNE, M.D., LL.D., F.R.S., Treasurer and Vice-President, in the Chair.

THE following were elected Members of the Royal Institution :—Mr. Arthur Salvin Bowlby, Sir Charles Cameron, M.D., M.P., Baroness de Knoop, Lord Romilly.

The Special Thanks of the Members were returned for the following donations to the Fund for the Promotion of Experimental Research at Low Temperatures :—

W. Morris Beaufort	£10
Mrs. Bloomfield Moore	£200
Professor Dewar..	£100
Sir Frederick Abel, Bart.	£50
Edward Frankland	£21
The Rt. Hon. Sir John Lubbock, Bart.	£20
John T. Brunner, M.P.	£50
The late Thomas Hawksley (per Professor Dewar)	£100
Charles Hawksley	£50

The Presents received since the last Meeting were laid on the table, and the thanks of the Members returned for same.

NOTICES OF BOOKS.

A Text-Book of Organic Chemistry. By A. BERNTHSEN, Ph.D., Director of the Scientific Department in the Chief Laboratory of the Baden Aniline and Alkali Manufactory, Ludwigshafen-on-Rhein; formerly Professor of Chemistry in the University of Heidelberg. Translated by GEORGE MCGOWAN, Ph.D. Second English Edition, revised and extended by Author and Translator. London, Glasgow, and Dublin: Blackie and Son, Limited. 1894. Crown 8vo, pp. 592.

THE very title-page of this work suggests matter for useful reflection. Need we wonder at the success of the German manufacturers of chemicals when they can find it worth their while to engage the services of so eminent a *savant* as Bernthsen, and can make it worth his while to resign the Chemical Chair at so distinguished a University as that of Heidelberg? This fact will appear the more striking if we reflect that the position of a professor is relatively higher in Germany than in England, seeing that in the former country he can teach according to his own insight, unfettered by the changing whims of examiners and "departments." We are especially glad that no attempt has been made to convert Dr. Bernthsen's admirable manual into a cram-book, as has sometimes been done by the translators of German scientific treatises.

The only error, in fact, which we can perceive relates to the production of aniline black (p. 542), which is said to be obtained by acting upon aniline with potassium *chloride* in presence of copper or vanadium salts. This is, of course, a printer's error for potassium *chlorate*. A few germanisms of expression and thought may be noticed. Thus we read (p. 492) of "sprit-blue." This is a common German expression for a colour which we should call "spirit-blue." The expression "it (tannin) *goes* into gallic acid when boiled with dilute acids" is scarcely idiomatic English. Malic acid (p. 257) is said to be found in "sorb-apples." We presume the writer means mountain-ash berries. It might have been added that the stalks of the garden rhubarb—or "pie-plant," as our American friends call it—is the most convenient raw material for the manufacture of malic acid. Citric acid, we are told (p. 267), occurs in "red bilberries." Does the author mean unripe bilberries, or the cranberry of central and northern Europe (Preisselbeere), a fruit which is acid beyond sweetening?

But putting on one side all these trifling peculiarities, we may congratulate author, translator, and publishers on the character of the book. After an introduction in which the author explains the calculation of formulæ, the determination of molecular weights and vapour densities, polymerism and isomerism, the nature of carbon, stereochemical isomerism, rational formulæ, homology, and the classification of organic compounds, Prof. Bernthsen proceeds to the specific part classifying organic compounds as methane derivatives, benzene derivatives, compounds with condensed benzene nuclei, and pyridine derivatives, to which are appended bodies of complex or unknown composition. The account of each substance is of course very concise, but strikingly clear and, as it might be expected, thoroughly accurate.

The book is to be warmly recommended, not merely to students, but to technical chemists, who will find it an invaluable key to the totality of organic chemistry.

The Institution of Mining and Metallurgy, London. Transactions. Vol. I., Parts 1, 2, 3, 4.

THE Institution of Mining and Metallurgy, whose offices are now at Broad Street House, New Broad Street, E.C., has been established with the object of advancing mining and metallurgical science; it consists of four classes, viz., Honorary Members, Members, Associates, and Students, the present total of all classes being 170. Every candidate for membership must be not less than thirty years of age, and shall have been for at least five years in a responsible position with regard to practical mining or metallurgy, and shall be at the time of his candidature in such a position. This at first sight appears to be a very stringent rule, but it is considerably modified by the proviso that a candidate is eligible if he prove to the satisfaction of the council that he is a fit and proper person to be a member.

Associates must be at least twenty-five years of age, and shall have been engaged in practical work for three years; while students must be over eighteen, and must have the intention of adopting mining or metallurgy as a profession.

The first preliminary meeting was held in January, 1892, when most of our well-known mining engineers were present; and it was agreed that the Institution be formed. Since that time meetings have taken place at stated intervals, and papers have been read and discussed on a variety of subjects connected with mining and metallurgy, though there seems to be a preponderance in favour of papers dealing in some way or another with the extraction of gold.

It is a curious fact that in a country so essentially dependent for its prosperity on mining as England is, the only society previously existing in connection with mining and metallurgy was the Mining Association and Institute of Cornwall, an institution the profession has every reason to be proud of, the only drawback being that it was too local.

The formation of this new institution has undoubtedly supplied a long-felt want, and we have every reason to hope and believe that it will prove to be of permanent and universal advantage to its supporters.

Commercial Fertilisers and Chemicals Inspected, Analysed, and Admitted for Sale in the State of Georgia up to June 20, 1894. Under the Supervision of the Hon. R. T. NESBITT, Commissioner of Agriculture of the State of Georgia, and Dr. GEORGE F. PAYNE, State Chemist, Atlanta, Georgia. The Franklin Printing and Publishing Co. 1894.

THE addresses, reports, recommendations, &c., comprised in this pamphlet are of value no doubt to the farmers of Georgia, but as everything relates to the special condi-

tions and soil of that fertile State, the results arrived at cannot, on the face of it, be of any far-reaching importance.

The United States Government have wisely instituted a large number of experimental stations and chemical laboratories all over the country for the purpose of fostering agriculture, and the work carried on at these stations is undoubtedly benefitting the districts where they have been started. There are herein a large number of analyses of soils and fertilisers of different kinds, and the actual commercial value of these is shown in a very plain manner.

It is interesting to note that the consumption of fertilisers in this State has been steadily rising for the last eighteen years. During the season 1874—1875 48,648 tons were used, and this has gradually crept up to 312,612 tons used in the season 1893—1894, that amount being the highest on record.

Catalogue of the Michigan Mining School, 1892—1894. Houghton, Michigan: Published by the Mining School. 1894.

Although this catalogue is for the years 1892—1894, its statements and calendar also apply to 1895 and 1896. It does not follow the usual lines of such a publication, but has been prepared to answer each and every question that has been asked the Director concerning the institution during the past seven years.

Full particulars are given as to the requirements for admission, the course of instruction, lectures, &c., and some sound advice is to be found in the paragraphs on "employment." The question has often been asked if he Mining School can promise employment to students on graduation. This is obviously impossible. The question of employment depends on too many factors to be promised several years in advance. The demand and supply is constantly varying, as well as the character and capabilities of the students themselves.

The cycle of depression and prosperity has been given as follows:—"A state of quiescence—improvement—growing confidence — prosperity — excitement — overtrading — convulsion—pressure — stagnation—distress—ending again in quiescence," when the cycle is again repeated. Education and training do not give qualities to any man: they simply sharpen and develop what natural abilities he may already have. If nature has not fitted him for a certain position, he is not very likely to obtain it, or at any rate to keep it.

The London Technical Education Gazette; being the Official Circular of the Technical Education Board of the London County Council. Vol. I., No. 1. London: Jas. Truscott and Son. 1894.

According to the opening statement, we find that this Journal will contain the official announcements of the Technical Education Board, which are of general interest to teachers and managers of the educational institutions in London, as well as to those seeking suitable technical instruction for themselves or their children. It will also contain all notices of scholarships and exhibitions offered by the Board, together with the regulations made by the Board respecting aid granted to schools and classes. The current number contains a considerable quantity of information of the above character, &c., which will probably be of interest to those for whom it is intended, but not appealing much to the general reader.

The National Society of French Horticulture.—This Society announces that it is organising an International Exhibition of the Products of Horticulture and of the connected Industries. It is to be held from May 22nd to 28th, 1895.

CORRESPONDENCE.

ESTIMATION OF CARBONATES AND CAUSTIC ALKALIS IN MIXTURES.

To the Editor of the Chemical News.

Sir,—Having had considerable experience in the use of phenolphthalein as an indicator in organic and inorganic solutions, I have been interested in the recent correspondence in your valuable paper upon the above subject by Messrs. Wilson, Aslanoglou, and Seyler.

Upon reference to the Chemical News (vol. liv., p. 28), it will be seen I describe a method devised for the estimation of caustic and carbonated alkali in the same portion of the sample taken, using phenolphthalein throughout, and I may say, if properly carried out, it will give accurate results. I have found phenolphthalein an excellent indicator when used under the essential conditions necessary for its successful application. But the difference in results obtained in this, as in other problems of analytical chemistry, can doubtless be traced to the different modes that chemists have of conducting methods of analysis consequent upon insufficient detail given as to the exact *modus operandi* of processes. The description of a method is generally so ambiguous that two chemists adopting it would often work quite differently as to weight taken, volume and strength of solutions involved, temperature, time of digestion, &c., &c.; and it is needless to comment upon the important bearing any irregularity in these stages of chemical manipulation may have upon the accuracy of the final results in many methods of analysis.

Quite recently the writer had occasion to submit a homogeneous material for analysis to four different well-known chemists, and the results obtained exhibited grave variations—in one instance a difference of 35 per cent in the quantity of a certain element being obtained.

Apropos of the great discrepancies in results obtained by different, more especially metallurgical, chemists, a well-known ironmaster of the writer's acquaintance used to jocularly remark that, "chemistry was a glorious uncertainty." And so it will remain until a uniform system is formulated for the conduct of methods of chemical analysis whereby personal equation will be altogether eliminated or reduced to a minimum.—I am, &c.,

H. Joshua Phillips,
Consulting Chemist.

Palace Chambers, Westminster Bridge,
London, November 19, 1894.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxix., No. 18, October 29, 1894.

Existence in Plants of Principles capable of being Split up, with Production of Carbonic Acid.—MM. Berthelot and G. André.—The authors have observed various facts concerning the chemical mechanism of vegetable respiration, as well as the methods employed for the determination. The question concerns the formation of carbonic acid and the absorption of oxygen by the leaves of plants. Their observations have been essentially directed towards the separation of the chemical phenomena properly so called from the biological phenomena. They have shown in former memoirs (*Annales de Chimie et de Physique*) that the leaves of various plants if heated to between 100° and 110° in a current of hydrogen evolve a certain proportion of carbonic acid. This process is

independent of biological phenomena. It is equally independent of the presence of oxygen, and proves the existence in the leaves of proximate principles capable of being easily decomposed and developing carbonic acid. If we repeat these experiments in presence of air, that is, of oxygen, always between the temperatures of 100° and 110°, we obtain proportions of carbonic acid which may amount to double those formed in the absence of oxygen. This fact proves that there exist in the leaves oxidisabie principles capable of being affected by air, with an especial formation of carbonic acid. The most recent experiments of the authors turn on the purely chemical formation of carbonic acid in consequence of the scission of immediate principles.

The Unity of Matter.—M. G. Hinrichs discusses this question in a work on the "Mechanics of Atoms."

Constitution of the Electric Arc.—M. Mascart.—This paper will be inserted in full.

The Gaseous Products Evolved from Wood Charcoal when submitted to a High Temperature with the Exclusion of Air.—M. Desmond.—The mean composition of the gaseous products of distillation are:—

Carbonic acid	9·14
Oxygen	0·26
Carbon monoxide	18·08
Hydrogen	49·11
Marsh-gas	16·04
Nitrogen	7·37
	100·00

Hence the reaction $C+CO_2=2CO$ hitherto admitted as the expression of the truth is much more complicated than the above formula indicates. The wood charcoal which has undergone the operation burns without odour or smoke and is in some cases preferable to ordinary charcoal. The antiseptic properties of the gaseous mixture are superior to those of carbon monoxide.

Temperatures of Transformation of Irons and Steels.—Georges Charpy.—The author concludes from his results that the point a_1 (690°—700°) corresponds to the transformation of the carbon characterised by the test of Eggertz, a transformation which much increases the hardness of the steel. The point a_2 (740°) corresponds to a transformation which slightly modifies the magnetic or mechanical properties. The point a_3 (860°) corresponds to a transformation which bears especially upon its magnetic properties.

On Kermesite.—H. Baubigny.—The results obtained by the author agree completely with those of H. Rose. Natural kermesite is an oxysulphide, Sb_2OS_2, and the assimilation to antimonial vermilion was made by Wagner. To this day the antimony oxysulphides have been prepared only by the dry way. They have been obtained in a crystalline state, but never in the moist way.

Superposition of the Optical Effects of Various Asymmetric Carbons in one and the same Active Molecule.—Ph. A. Gaye and M. Gautier.—The optical effect of a non-symmetric carbon of amyl oxide answering to the formula is $\alpha_D=+0{\cdot}27°$ (approximate value), so that in virtue of the principle of algebraic superposition, amyl with two identical active carbons ought to give a double deviation, that is, $\alpha_D=+0{\cdot}50°$, for $L=0{\cdot}5$ d.cm.

The Saturated Hydrocarbons with Active Amylic Radicles.—Ida Welt.—The author attempts to determine the rotatory powers of some terms of the series of active hydrocarbons containing the amyl radicle.

Determination of Alcohols in the Essential Oils.—C. Fabre, Garrigou, and Surre.—The name essential oils is here given, not to the products usually so-called, but to a residue left in the rectification of alcohol.

No. 19.

The Volatilisation of Carbon.—H. Moissan.—This memoir will be inserted in full.

Researches on the Mercury Nitrates.—Raoul Varet.—The author has measured the formation heat of the mercury nitrates, hitherto unknown. In the dissociation of neutral mercuric nitrate by water, of all possible reactions this is the least endothermic. Nitric acid, like the sulphuric, picric, acetic, and oxalic acids, and unlike the hydrochloric and hydrocyanic acid, when combined with mercury oxide, is displaced entirely, or to some extent, by these latter.

Presence of Methylsalicylic Ethers in some Indigenous Plants.—Em. Bourquelot.—The plants in which methylsalicylic ether or methyl salicylate has been already recognised are all exotic. The author has now found the same principle in some indigenous plants belonging to the genera *Polygala* and *Monotropa*. Such are *Polygala vulgaris*, *P. depressa* and *calcarea*, and *Monotropa hypopitys*.

MISCELLANEOUS.

A Remarkable Phenonenon of the Adhesion of Aluminium and some other Metals to Glass.—Ch. Margot.—The author observes that aluminium has a great power of adhesion to glass, so that designs can be made upon moist glass with an aluminium pencil which cannot be removed with any mechanical agency. If the metallic aluminium is dissolved away with acids, the design remains visible like an etching. Hence the author concludes that the metal has a chemical action upon the basic silicate. Certain natural silicates behave like glass; quartz, emerald, topaz, and corundum behave like silicates, whilst there was no action upon diamond. Magnesium acts like aluminium, cadmium rather more slightly, and zinc still more feebly.—*Archiv. des Sc. Phys. et Naturelles de Genève* and *Zeit. f. Anorganische Chemie.*

MEETINGS FOR THE WEEK.

Tuesday, 26th.—Institute of Civil Engineers, 8.
—— Medical and Chirurgical, 8.30.
—— Medical, 8.30.
—— Photographic, 8.
Wednesday, 28th.—Society of Arts, 8. "Experiments in Aeronautics," by Hiram Maxim.
—— British Astronomical Association, 5.
Friday, 30th.—Royal, 4. (Anniversary).

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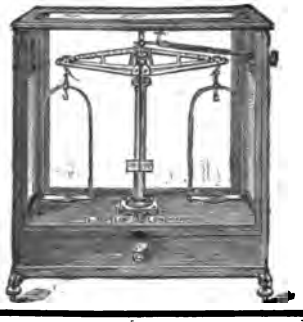

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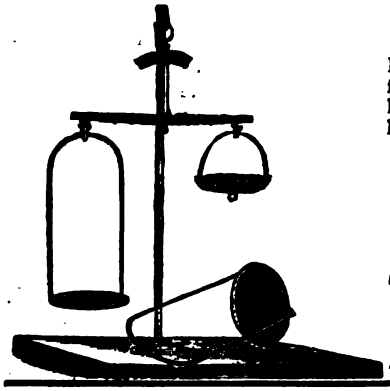

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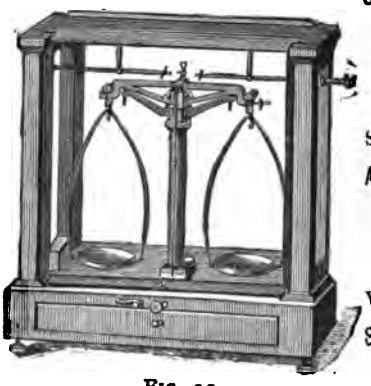

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THE CHEMICAL NEWS.

VOL. LXX., No. 1827.

I.—ON SOME NEW METHODS OF OBTAINING PLATINOCHLORIDES. II.—PROBABLE EXISTENCE OF A PLATINUM SUB-CHLORIDE.

By M. CAREY LEA.

THE methods now in use for obtaining potassium platinochloride are:—1. Heating platinic chloride to 250—300 C., and treating with potassium chloride. 2. Passing sulphurous acid through a boiling solution of platinic chloride and treating with potassium chloride. To these older methods Thomsen has added: 3. Treatment of potassium platinichloride with cuprous chloride.

All these have objections. With 1 it is not easy to obtain a uniform conversion. 2 requires to be very closely watched to catch the exact moment at which the change is complete. 3 is liable to a vexatious reverse action by which platinous salt is re-converted into platinic salt at the expense of the cupric chloride present. Thomsen mentions this danger as occurring in hot solutions. It probably depends, however, more on concentration than on temperature. The larger the proportion of cupric chloride present in any solution the greater the tendency to reversal. In one case a half litre of mother water containing platinous salt was set aside for spontaneous evaporation. In a few days large crystals of the red salt began to form; in a few days more, instead of these increasing, there was not a crystal of the platinous salt left.

These objections led me to look for something different. I have found two methods, either of which give good results.

First Method.—Potassium Acid Sulphite.

Potassium platinic chloride is to be moderately heated with solution of the acid sulphite; convenient proportions are: platinum salt 12 grms., acid sulphite 9 grms., water 160 c.c. The mixture can be placed over a hot water-bath in a covered vessel and left to itself. The reduction takes about ten to twelve hours, and is known to be complete when the solution has a pure red colour free from yellow. The cover is then removed, and the liquid evaporated to the crystallising-point.

If, as may happen, the red chloride and the other salts crystallise out together, it is best to re-dissolve them by heat in a small quantity of water saturated with potassium chloride. The red salt then crystallises out first.

Second Method.—Alkaline Hypophosphites.

By reason of its great reducing powers a very small proportion of alkaline hypophosphite is capable of converting the yellow platinum salt to the red; theoretically one part of hypophosphite should reduce nine or ten parts of platinum salt. We can hasten the operation somewhat by using an excess of hypophosphite, but then must work at a lower temperature. Both methods will be given.

In using an excess of hypophosphite it is convenient to take 10 grms. of platinum salt, 2 grms. or even more of potassium hypophosphite, and 600 c.c. of water. These are placed in a flask and very gently heated. The best temperature is 66—70° C.

There is a very easy way of obtaining this temperature and of keeping it perfectly constant for any length of time by taking an ordinary water-stove of the kind in which a chamber is surrounded on five sides by water. Such a stove is to be furnished with a Kekulé constant level, regulated to keep the water-jacket half full. If now the heat is turned on so as to keep the water gently boiling, it will be found that solutions placed *on the top* maintain a perfectly steady temperature, varying from 55° to 72° C. according to the shape of the vessel, but constant for any one shape. The lowest temperature, about 55°, is obtained with an open flat porcelain basin. It rises gradually as the shape of the vessel tends more to check evaporation. When a litre flask has about two inches of solution, the temperature will remain steady at about 66°, and this temperature is very suitable for the treatment just described.

Even with this excess of reducing agent ten or twelve hours will be required. The solution must not be allowed to evaporate to less than one-half its original bulk.

The completion of the operation is known by the solution showing a perfectly pure ruby-red colour. The slightest shade of orange indicates the presence of the yellow platinic salt. It is much safer to allow the solution to evaporate spontaneously. If evaporated by heat there is always a chance that the reduction may go too far.

There is not much to choose between these two methods. The first, with acid sulphite, is the safest, because there is no danger of carrying it too far. On the other hand, in the second method the red salt separates more easily and completely in crystallising.

On the whole the method which I prefer is to keep down the hypophosphite and use a higher temperature and longer heating. For this, a weighed quantity of platinum salt may be placed in a flask with 30 c.c. of water for each grm. of the salt and a quantity of potassium hypophosphite equal in weight to one-ninth of the platinum salt. The flask is to be placed in a water-bath which is kept at 80° to 90° C. In consequence of the small proportion of hypophosphite the action is slow, requiring about eighteen or twenty hours for complete conversion. No attention during this time is required, and the advantages are that the solution becomes sufficiently concentrated to crystallise on cooling, and that the very small quantity of foreign matter introduced renders it easy to obtain a pure product.

At 100° C. the reduction to red salt takes place in about fifteen minutes. This method is practicable, but requires great circumspection. If the boiling is continued a little too long, the solution suddenly turns brown; the reduction has gone too far.

If a quick reduction is desired it is better to use an acid sulphite as a reducing agent, and the following method gives satisfactory results:—In a flask is placed 300 c.c. of water, 24 grms. of potassium platinic chloride, 12 grms. each of potassium acid sulphite and potassium chloride. Sodium acid sulphite should not be used. The introduction of sodium salts interferes with the crystallisation, not indeed with the first crop of crystals, but later. These are made to boil rapidly together for twenty-five minutes, reckoned from the time when actual boiling begins. The solution is allowed to cool, filtered if necessary, and placed in a large flat-bottomed glass or porcelain vessel. In a day or two the red salt will commence to form large crystals. The addition of the potassium chloride causes the red salt to crystallise out first.

It has seemed worth while to give these methods in some detail, because the red platinum salt is likely to find a constantly increasing use in photography, not only for platinum printing, but as a substitute for gold in toning. There is no doubt that platinum is a much better metal for toning silver prints than gold. Its tones are better, and its action is much more reliable.

By all these methods this beautiful salt is obtained in fine ruby-red prisms.

Probable Existence of a Platinum Sub-Chloride.

If in obtaining potassium platinochloride with the aid of a hypophosphite in excess the heat is continued after

complete conversion to the red salt, the solution in a few minutes changes from red to dark brown. The substance which gives the solution this dark brown colour exhibits the following properties:—

It is very deliquescent and cannot be crystallised. There is no satisfactory method of separating it from the other substances in solution. An oxide of platinum appears to be precipitated by the addition of potash, and this precipitate when freshly made dissolves easily in hydrochloric acid, but if it is thrown on a filter and washed, almost the whole of it runs through. This difficulty, it is true, can be avoided by washing with a dilute solution of potassium chloride. But the precipitate after washing is no longer soluble in hydrochloric acid, except that the acid dissolves out a little protoxide derived from the red salt, some of which is apt to escape reduction.

The brown solution exhibits the following reactions:—

Hydrochloric acid has no effect.

Nitric acid decolourises it.

Potash produces a brown precipitate soluble in an excess of the precipitant.

Ammonia a brown precipitate insoluble in an excess.

The solution itself is opaque by reason of its intense colour. When largely diluted it is yellowish brown and perfectly transparent.

From the method of obtaining this substance there seem to be only two possible explanations of its nature. First, that it is metallic platinum in a state of solution; this is decisively negatived by the reactions just described. Second, that it is a chloride containing less chlorine than platinous chloride; therefore a sub-chloride. If the precipitate obtained by potash could after washing be dissolved in hydrochloric acid, its constitution could easily be determined. But during the washing it seems to be converted into metallic platinum.

I have noticed that when a solution of the ruby-red salt $2KCl,PtCl_2$ is spread on paper and exposed to sunlight it does not blacken, but assumes a yellowish brown colour; it would seem, therefore, that light acts upon it much in the same way as a hypophosphite, reducing it probably to a sub-chloride. If the reduction was to metallic platinum, this would be shown by the production of an intense blackness.

In all this, analogy with silver salts is unmistakable. Pure silver chloride is not reduced to metal by the action of light, for after exposure it yields nothing to nitric acid. Both metals seem to form sub-chlorides, the oxides corresponding to which are very unstable.—*American Journal of Science*, xlviii., Nov., 1894.

ON AN EXTENSIVE CASE OF ARSENICAL POISONING IN LUGANO.

By Dr. E. VINASRA.

The poison seems to have been unknowingly consumed as an impurity in common salt. The first attack of poisoning took place in Brissago, on Lake Maggiore, in the Asilo Infantile, apparently an orphan-house. On September 24th, 1892, a majority of the children, shortly after dinner, were seized with violent vomiting. An examination of the water proved the absence of zinc (from the galvanised iron cistern). Further investigations showed that no poisonous plants had been added to the soup in mistake for parsley.

The next day the children were again attacked with vomiting. In some samples of table-salt used in the neighbourhood, arsenic was found to the extent of 0·5 per cent. It must be remembered that in Lugano, as in the rest of Switzerland, salt is a government monopoly, supplied to the public only by certain agents. Of twenty-six samples obtained at Brissago, twelve were found to contain arsenious acid, but in very different proportions, ranging from 1/100,000th grm. to 0·5 grm. per cent—a proof that the arsenic was not an original impurity traceable to the salt-works, but must have been subsequently introduced. All the poisonous samples were traced to the dépôt in the village of Brissago, and had been taken from a single sack. Arsenic was found in greater or less quantities up and down the houses, especially in a residue of a powder taken from a large iron mortar. It seemed probable that the dealer must have ground up coarse cattle-salt in the iron mortar for the purpose of selling it as fine salt. But whence the arsenic? There seems no reason to suspect that the keeper of the salt-dépôt was aware of the presence of arsenic in the salt which he supplied. But the arsenic was present in the samples referred to, and in the remains of a man who had succumbed to the poison. The total number of persons affected was 128. There was 1 death, 14 cases of severe illness, 77 of persons who suffered from the consequences for at least a fortnight, and 36 who felt merely transient illness.

The inference to be drawn is the necessity for extreme care in the storage of arsenic, which, though by no means one of the more violent poisons known, is more than any other liable to escape observation. The salt-agent at Brissago was a drysalter, and, so far as we can judge from the facts, a man of careless habits. —*Chemiker Zeitung*.

ON COLLOIDAL SILVER.

By E. A. SCHNEIDER.

A communication was made some time ago to the *Berichte*, on the Solutions of Colloidal Silver in Ethylic Alcohol. Since that time further experiments have been made on the solubility of silver in organic liquids.

Each c.c. of the organosol, $Ag(C_2H_5OH)$, 3·424 grms. silver per litre, was mixed on a test-tube with 5 c.c. of the solvent. At this concentration it was easy to observe whether coagulation ensued or not. Only in some cases the organosol in question was prepared in a pure state with some more easily procurable solvent. Otherwise we were content with the observation whether coagulation ensued or not, because it could hence be inferred with some certainty whether the organosol concerned was capable of existence or not.

No coagulation was occasioned by propylic, isobutylic, and tertiary butylic alcohols, cetylic alcohol in an alcoholic solution, ethylenic alcohol, glycerin, and phenol.

Coagulation took place in a few hours on addition of trimethylamide and pyridine.

Immediate coagulation was effected by isopropylic, normal and secondary butylic alcohols, trimethyl carbinols, heptylic alcohol, octylic and allylic alcohols, erythrite, octane, amylene, formal aldehyd, œnanthol acetone, ethylic ether, glacial acetic acid, benzene, benzylic alcohol, meta-kresol, triethylamine, dimethylamine, diethylaniline, and quinoline.

The solutions in which no coagulation took place were observed for several months in succession. It was observed that after fourteen days phenol began to exert a coagulating effect, and in a week later the coagulation was distinctly visible. In a month after the commencement of the experiment indications of coagulation were seen in the solutions, mixed with propylic alcohol and tertiary butylic alcohol. After two months more coagulation had set in in all the solutions.

Only the solution occasioned by glycol was soluble in water, whilst in all other cases the coagulum dissolved in water with its original colour.

The organosol $Ag(C_3H_5[OH]_3)$ was obtained by evaporating down a mixture of equal volumes of the organosol $Ag(C_2H_5OH)$ and glycerin, in a vacuum over sulphuric

acid. No sedimentation was perceived in it after the lapse of several months.

A systematic study of the behaviour of the colloids with organic solvents promises interesting results if it is practicable to detect a certain regularity.

It was already observed that various colloids did not behave alike with the same solvents. So far it has not been found possible to obtain an organosol of stannic acid in ethylic alcohol, whilst an uncommonly stable organosol was obtained with glycerin.

In my former communication on colloidal silver, the properties of the colloid in a perfectly dry state were not mentioned, wherefore they may be noticed at present.

A large quantity of the organosol $Ag(C_2H_5OH)$ was coagulated with absolute ether, the precipitate washed with ether by decantation, and dried *in vacuo* over sulphuric acid. The dry colloid had a green metallic lustre. The loss on ignition was 4·5 per cent. On heating, an empyreumatic odour was recognised. In an atmosphere saturated with watery vapour it took up 50·52 per cent weight in the course of three days.

The colloid precipitated by ether, and then dried, dissolved entirely in water. —*Zeitschrift fur Anorganische Chemie.*

DETERMINATION OF NITROGEN IN NITRATES, NITRO-, AND NITROSO-COMPOUNDS IN THE WET WAY.

By MARTIN KRÜGER.

In nitrogenous bodies in whose mols. the nitrogen atoms are combined with oxygen it is admitted that neither the original method of Kjeldahl nor the modification proposed by Wilfarth gives useful results. Even when benzoic acid is added to the acid mixture as directed by von Asboth we obtain with the nitrates only approximate values.

Jodlbauer instead of benzoic acid uses the readily nitrised sulpho-phenolic acid, and converts at the same time the nitro-substances formed at first into amido-compounds by means of a reducing agent. He therefore treats the nitrates with a mixture of sulphuric acid and sulpho-phenolic acid, to which he adds at the same time zinc-powder and some drops of a dilute solution of platinum chloride. The method gives very good results, but it must be regarded as a misfortune that the nitric acid, in order to be reduced, must be combined as a nitro-group to an aromatic complex not easily destroyed.

Dafert reduces nitro- and nitroso-substances in oil of vitriol or in a mixture of alcohol and oil of vitriol by zinc-powder and thus destroys the amido-bodies formed with Kieusler's acid mixture (consisting of 1 litre concentrated sulphuric acid and 200 grms. phosphoric anhydride), with the addition of a little mercury.

The author used in his analyses a strong hydrochloric solution of stannous chloride containing 150 grms. tin per litre and also metallic tin, preferably precipitated by means of zinc from solutions of stannous chloride. The amido-substances thus obtained from nitro- and nitroso-compounds were then oxidised with potassium bichromate and concentrated sulphuric acid according to the process described in *Berichte*, xxvii., p. 609.

The determination of the nitrogen in nitro- and nitroso-compounds and nitrates is hence conducted as follows:—

0·2 to 0·3 grm. of the substance in question is mixed in a round flask with about 20 c.c. of water, or in case of bodies sparingly soluble in water with 20 c.c. of alcohol, to which are then added 10 c.c. solution of stannous chloride and 1·5 grm. spongy tin. The flask is then heated over a small flame until the mixture is decolourised and the tin is dissolved. When this is effected, and when the liquid is cooled, and when alcohol, if present, has been expelled, 20 c.c. of concentrated sulphuric acid are carefully added, the mixture is heated until vapours of sulphuric are given off in abundance. When the solution is cold the amido-substance obtained is oxidised with rather more than the calculated quantity of bichromate, as stated in the former communication.

In case of nitro-substances which escape from acid solutions along with watery vapours, the alcoholic solution mixed with stannous chloride and tin is heated first on the water-bath, but after the reduction is complete the alcohol is expelled over an open fire. It is more convenient and suitable to heat volatile compounds with the solution of stannous chloride alone in a closed tube which is set in a vessel full of boiling water.

The determination of nitrogen in nitrates is much simpler, as the oxidation with bichromate is of course superfluous. As soon as the metallic tin is dissolved in the hydrochloric solution of stannous chloride in gentle ebullition, the reduction of the nitric acid to ammonia is completed, and the latter can be ot once distilled off from the solution after dilution and the addition of alkali in excess. —*Berichte der Deutsch. Chem. Gesell.*, xxvii., p. 1633.

ACTION OF THE ELECTRIC ARC UPON THE DIAMOND, AMORPHOUS CARBON, AND CRYSTALLINE SILICON.

By HENRI MOISSAN.

Diamond.—In a memoir published in the *Annales de Chimie et de Physique*, 1847, Jacquelan demonstrated that diamond is transformed into graphite if heated in the midst of the electric arc. It is easy to render this experiment visible in an entire amphitheatre by adopting the following arrangement:—

We project upon a screen the image of the two carbons between which an arc of small intensity is to be made to play. One of the carbons very slightly hollowed supports a diamond either cut or rough of from 100 to 200 m.grms., the image of which is projected very distinctly by means of an intense electric light. The carbons are approached to each other slowly, so that the arc may play on the side and heat the diamond slowly, lest it should burst at the outset. When the temperature has been sufficiently raised, the diamond is heated to incandescence, and we soon see it sprout without fusion and become covered with black masses consisting entirely of graphite. If examined after the experiment the graphite appears in the form of hexagonal laminæ, separate from each other, and capable of easy conversion into graphitic oxide by the action of the mixture of potassium chlorate and nitric acid.

At the temperature of the arc, even if not very powerful, the stable form of carbon is therefore graphite.

In numerous experiments I have had occasion to heat diamonds, rough or cut, enclosed in a lined crucible, to the temperature of the oxygen blowpipe (2000°). Under these conditions the diamond has been sometimes covered with a very adhesive black coating, which disappeared slowly in the mixture of potassium chlorate and nitric acid, but I have never obtained graphite.

On burning Cape diamonds to obtain their ash for analysis, I have sometimes seen the diamond, in the moment of combustion, become covered with a black layer, a fact formerly observed by Lavoisier, and since verified by Berthelot.

Boron.—If we place in the electric arc pure amorphous boron prepared by means of magnesium, and conducting the experiment as just described, we see the boron become red, surrounded with a large green halo, and then disappear without presenting any phenomenon of fusion. After the experiment we find at the extremities of the electrode black masses of a melted appearance presenting some crystalline points and consisting of a carbon boride of a very simple composition.

In this latter experiment it is very important to have the electrodes of the purest carbon possible. If the mass of boron is rather large at the same time as the boron and carbon combines, boric acid may be formed, which melts with rapidity and enters into ebullition, but may be easily removed by means of boiling water.

Silicon.—Crystalline silicon, prepared by the method of H. Ste.-Claire Deville, is placed between the two carbons. As soon as the arc plays we see very distinctly on the image projected the silicon enter into fusion and then into real ebullition. When the electrodes have cooled we find on their summit in the midst of the graphite formed pale green crystals of carbon silicide.

At this high temperature boron and silicon combine readily with carbon.—*Bull. Soc. Chim. de Paris*, xi.-xii., p. 993.

NOTES ON THE HARDENING OF MORTAR.*

By W. P. MASON.

The following is extracted from the graduating thesis of Mr. J. A. McPherson, of the class of 1894, Rensselaer Polytechnic Institute, the work having been done in my department:—

It is common belief among builders that it is better practice to mix lime mortar and let it lie in a heap some days previous to use, rather than to employ it directly after preparation. In order to test this point, samples of mortar were taken, on successive days, from two separate heaps of large size; briquettes were made therefrom, and, after an interval of some weeks, were broken for estimation of tensile strength with the following results:—

	Days in heap after mixing.	Days exposed to air as a briquette.	Average breaking wt. in pounds per sq. in.
Mortar No. 1 ..	3	50	34·6
„ „ ..	4	49	38 6
„ „ ..	6	48	38·1
„ „ ..	7	46	39·3
Mortar No. 2 ..	4	48	36·0
„ „ ..	5	47	38·0
„ „ ..	6	46	41·2
„ „ ..	7	45	41·5

As concerning the formation of calcium silicate through the action of the lime upon the sand, the amount of such formation was found exceedingly small, even after great intervals of time.

After extended experiments with mortar taken from the old Van Rensselaer mansion at Albany, built about 1760, and with mortar from a very ancient tower in the valley of the Lahn, the quantity of calcium silicate found therein was 0·34 per cent of the total weight of the mortar, an amount altogether too small to be considered as a factor in the hardening of the mortar.

The influence of tempering hydraulic mortar with water containing sugar (one-half pound of sugar to one gallon of water) is shown by the following averages, the mortar used having a tensile strength when tempered with pure water of 63 pounds per square inch.

Average tensile strength of sugared briquettes exposed to water during 38 days was 62·75 pounds.

Similar briquettes exposed to air during same period was 65·4 pounds.

There is, therefore, a gain of 3·8 per cent over the water-tempered mortar in cases where the mortar is used in air, but no advantage when the mortar is intended for sub-aqueous work.

In South America there has been occasional use of bullocks' blood for tempering hydraulic mortar. In view of this, a number of experiments were made with the same mortar which was used in the sugar experiments, but the tempering was made with bullocks' blood diluted with one-third its volume of water. The resulting briquettes set somewhat more quickly, and were very hard and firm. Their average tensile strength was—

After exposure to water during 37 days, 68·3 pounds.
„ „ air „ „ „ 69·8 „

Thus showing a gain over the water-tempering of 10 per cent for the briquettes set in air.

* From the *Journal of the American Chemical Society*, November, 1894. Read at the Brooklyn Meeting, August 16, 1894.

BRIEF COMMUNICATION ON A NEW PROCESS FOR THE TREATMENT OF AURIFEROUS ORES WITH BROMINE, AND RECOVERY OF THE BROMINE EMPLOYED.

By C. LOSSEN.

Various procedures have been made known of late for the treatment of auriferous ores with bromine, especially as a substitute for chlorine.

Although it was found practicable to reduce the consumption of bromine to a minimum (down to 1¼ lbs. per ton), its application on the large scale has not become general, and the operators always returned to chlorination.

After prolonged experiments I have succeeded in developing a process for the recovery of the bromine used in the extraction of the gold, so that the working cost is considerably reduced.

The simplest and cheapest method of liberating bromine from any compound is by means of the electric current. A solution of potassium bromide is decomposed by the current, so that, on introducing a diaphragm of asbestos cloth, a solution of bromine in potassium bromide is separated at the positive pole, whilst potassium hydroxide is produced at the negative pole. By the diffusion of both solutions through the diaphragm there are always formed certain quantities of hypobromites and bromates. But if such a solution is decomposed without the introduction of a diaphragm there results an alkaline liquid, which of course cannot contain free bromine, but which has the property of dissolving leaf-gold.

I reserve a more complete account of the method, and will here merely give the principal points of the process as about to be introduced at a mine in Oregon.

The ore, green or roasted, is mixed with an alkaline solution of bromine in a cylinder, which is maintained in rotation until all the gold is dissolved. If the mass is no longer alkaline a second portion of the bromine solution is added before the mass is introduced into the filtering vessels. The gold is not precipitated, but remains in solution as an aurate, whilst iron and other metallic salts remain as hydroxides and the bromine is dissolved as potassium bromide. The filtered solution then flows, for the recovery of the gold through tanks filled with a mixture of iron and carbon, or coke, whereby the gold is entirely precipitated. The solution, free from gold and containing chiefly potassium bromide, flows into long troughs, in which it is decomposed by the electric current, and can then, as a solution of alkaline bromide, serve for the treatment of fresh quantities of ore. — *Berichte Deutsch. Chem. Gesell.*

University of Dorpat.—According to the *Chemiker Zeitung* not only Prof. Dr. Dragendorff, but Dr. Rud. Kobert, Ordinary Professor of Pharmacology and of the History of Medicine, will shortly vacate their chairs at the University of Dorpat, as on and after January 1 all lectures must be delivered in the Russian language.

ACTION OF LIGHT ON BACTERIA AND FUNGI.*

By Professor H. MARSHALL WARD, D.Sc., F.R.S., F.L.S.

(Concluded from p. 252).

Now the special interest of this new line of investigation I have been pursuing turns largely on the fact that this particular bacillus, which is not uncommon in the river Thames, is by no means a very sensitive one to light, as compared with several others known to me.

For if such a form can be so easily destroyed in a few hours by the light from an April sky passing through several inches of water and two sheets of glass, we may fairly conclude that more sensitive forms are easily destroyed in the river, exposed to the rays of a summer sun during the long days of June, July, and August.

As matter of fact—and the fact has been confirmed by many other observations—I found that in spite of the high temperature of the summer of 1893, which we should expect to favour the development of bacteria, and in spite of the river being low, and presumably more concentrated as a food solution for bacteria; and, further, in spite of the fair expectation that, per unit of volume, the water ought to contain more bacteria than during the cold months of October, November, and December, when the river is more diluted, and so on; *the number of bacteria per cubic centimetre is decidedly and markedly less in the summer than in the winter months!*

This is very clearly shown by the statistical curves I now throw on the screen.

[Curves of average number of bacteria per 1 c.c. of Thames water in August, October, and December, 1893.

Now I am perfectly aware that it has been the custom to regard this well-known fact as due to a series of causes of quite different kinds, the action of which may or may not co-operate in bringing about the variations in the quantities of bacteria per unit of volume in such a river as the Thames, but I submit to you whether, in view of the new facts I have elicited, it is not at least highly probable that the increased intensity of the light, acting during a longer period through the summer days, is a very powerful agent in keeping down the numbers of these bacterial and fungoid organisms in the river.

It must be remembered that in my experiments, although I get such pronounced positive results wherever I employ water enclosed in glass vessels as the screen, I certainly do not get anything like the effects that the same exposures give *if I dispense with the glass* of the containing vessels, mirrors, &c.; for even a thin plate of glass is a decided obstruction to the rays at the violet end of the spectrum, and so I have to record positive results considerably below what I should get if the light from the sun and the blue sky reached the organisms through the medium of water only. In the experiments I am now continuing, no glass whatever is employed, and the light is not allowed to traverse or be reflected from any but quartz or metal surfaces.

Unfortunately, we are as yet but scantily informed as to how far the blue-violet rays penetrate into deep water, but experiments by Regnard, Fol, Forel, and others have shown that they do penetrate to a considerable depth. Fol, for instance, showed that some light gets down as far as 400 metres, and Forel got effects with photographic paper at 45 to 100 metres in the Lake of Geneva, and so on, depths quite sufficient for my purposes, though I hope that more accurate and extended information will yet be obtained on the subject.

Some consequences of this view of the destruction of bacteria in water by light are of the utmost importance. For instance, we can understand how the typhoid bacillus, if it falls into turbid dirty water in the summer, may multiply at the high temperature and at the expense of the food-materials dissolved from the organic matters in suspension, and this at its pleasure, so to speak, because the suspended particles of matter, to which the turbidity is due, favour it in (1) supplying it with food, (2) absorbing heat and helping to raise the temperature of the water, and (3) *impeding the penetration of the destructive light rays.*

The results of the investigation also suggest explanations for many other facts which have hitherto been unexplained. Thus Pasteur and Miquel pointed out some time ago that the germs floating about in the air *are for the most part dead!* This we can explain by the bactericidal action of the sun's rays, just as we can also probably explain the freedom from germs of the Alps.

Again, Martinaud has shown that certain yeasts which normally vegetate on the exterior of ripening grapes, are destroyed if the sunshine is very intense; and Giunti has stated that the ingress of sunlight hinders acetic fermentation, a process which depends on the life-processes of a well-known bacterium.

I have myself observed many cases where the free access to light is inimical to the germination and development of fungi of various kinds, and Elfving has recently studied very thoroughly the action of light on a common mould-fungus with astonishing results, quite intelligible in the light of the foregoing investigation. These matters are of more significance in connection with the spread of the potato and other diseases in dull warm weather than I have time to explain here; and probably have a wide bearing on the deterioration of forest and agricultural soils exposed to the sun, as well as on many questions of greenhouse practice too numerous to even mention.

They also bear on the question of sun-baths and the whole hygiene of sunshine treatment, as well as sunburn, "tanning," snow-blindness, &c. But still more startling probabilities must be looked at, though I have brought my lecture now to a point where I must remember that your patience in listening to me should not be abused.

We have seen that in my experiments certain colour-screens are efficacious in so cutting off the access of the destructive rays, that the protected germs, bacilli, fungus-spores, &c., can germinate and develop as easily as if no light at all was playing on them. It struck me during the progress of these experiments that *just such colour-screens are very common in Nature*, in cases where just such spores and tender growing cells are compelled to begin or carry on their vegetative processes in the light. This led me a short time ago to publish the following opinions based on the facts even then to hand:—It seems likely that pollen-grains, many fungus-spores, and a large number of such organisms as are exposed to light, are provided with the colour-screens they possess, *and which screens are usually red or orange, or some shade such as cuts out the blue-violet rays*, as an adaptive protection against the injurious rays of light. It is but an extension of this to see in the green chlorophyll-screen of all our ordinary plants in part a protection against the blue-violet rays of ordinary sunlight, the ingress of which to the cell-contents would bring about destructive changes of the order discussed in this lecture; but we must not forget that the chlorophyll apparatus is more complex than this, and is essential to the process of carbon assimilation, absorbing and making use of the energy derived from the red-orange rays.

In conclusion it is impossible to put forward in a single lecture all the results obtained, and still less the bearings of these results and the experiments now being continued. I can merely say that there is evidence to show that the slow and continued action of even comparatively low intensities of light so act on these bacteria I am working with that even where they are not killed, but only partially injured by the inimical rays, their behaviour is so altered that the resulting growths are perceptibly different from those of the same organisms not exposed to light,

* A Lecture delivered at the Royal Institution of Great Britain, April 27, 1894.

that their powers of fermenting organic substances are interfered with, and that various profound morphological and physiological changes are induced in them. The bearings of these matters, which are very complex, and the investigation of which is full of peculiar difficulties, moreover, are so important in regard to various questions concerning fermentation, the germ theory of disease, and other departments of bacteriology, that I have no hesitation in saying that no subject more vital to the interests of mankind exists in the whole domain of biological science.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 1st, 1894.

Dr. Armstrong, President, in the Chair.

Messrs. H. Davies, J. T. Hewitt, R. E. Hughes, and E. Brooke Pike were formally admitted Fellows of the Society.

The President having pointed out that the Certificates of Candidates for election are now always printed *in extenso* and circulated in the *Proceedings* before the date of ballot, it was unanimously resolved by the Meeting that the reading of only the names of Candidates should be regarded as reading the Certificates.

Certificates were read for the first time in favour of Messrs. Frederick John Allen, Phœnix Chemical Works, Poplar; George H. Allibon, Earlsfort, Strandmillis Road, Belfast; John Allport, M.A., 32, Lancaster Park, Richmond, S.W.; Samuel William Allworthy, M.A., M.D., Mosaphir, Cavehill Road, Belfast; Stephane Barlet, B. ès. Sc., 47, Bassett Road, W.; James Boulton, Crafford Mills; D. R. Boyd, B.Sc., Mason College, Birmingham; John Samuel Strafford Brame, 36, Howard Street, Gloucester; James Bruce, 10, Selwood Terrace, Fulham Road, S.W.; George William Burman, 9, Ebor Terrace, Woodhouse Hill, Hunslet, Leeds; William Bush, Eastgate Villa, Chepstow Road, Newport, Mon.; Ezra Catherall, Harecrofts, Wilsden, Bradford; Arthur Herbert Coote, 8, Laurel Terrace, Bradgate Road, Catford, S.E.; John William Deakin, Northwich; William Michael Doherty, Robert Street, Marrickville, Sydney, N.S.W.; Lewis Benjamin Saltwell Dutson, 14, Vicarage Place, Walsall; John Garwood Everett, 29, High Street, Windsor; Alfred Greeves, Southlands Training College, Battersea, S.W.; John Hall, Spring Bank, Leftwich, Northwich; Edward Haworth, B.Sc., Hyndburn Bridge, Clayton-le-Moors, Accrington; Albert Helms, Ph.D., 8, Bridge Street, Sydney, N.S.W.; Alexander Frederick Hogg, M.A., 73, Stanhope Road, Darlington; George Cecil Jones, Fylton, Bristol; Bevan Lean, B.A., D.Sc., Dalton Hall, Victoria Park, Manchester; W. H. Lewis, B.A., The Laboratory, Exeter School; George William MacDonald, B.Sc., 15, Stanley Gardens, N.W.; Charles James Shaw Makin, 51, Earls Court Square, S.W.; James McCutcheon, Marchmont, Lanark, N.B.; Charles Butterworth Newton, Gas Works, Rotherham; Thos. Ormerod, Sackville Street, Burnley; James Proude, 13, Oak Terrace, Halifax; Gerald G. Quinn, 7, Albert Street, Newcastle, Staffs.; David Gibson Riddick, Stores Department G.E.R., Stratford, E.; Alfred George Scorer, Abercorn Lodge, Upper Hamilton Terrace, N.W.; Claude Smith, Havering, Romford, Essex; Albert Taylor, 2, Torkington Street, Edgeley, Stockport; William G. Wagner, 101, Leadenhall Street, E.C.; Robert Waterhouse, 101, Leadenhall Street, E.C.; William L. Warren, 12, Westland Row, Dublin; Christopher Wilson, The Grammar School, Manchester; Robert Hanbury Wilson, Washing Stocks Farm, Bromsgrove, Worcester; Alexander Poole Wilson, Maypole House, Knocklong, Co. Limerick; James Young, 4, Plumstead Common Road, Woolwich.

Of the following papers those marked * were read:—

*54. "*The Electromotive Force of Alloys in a Voltaic Cell.*" By A. P. Laurie, M.A.

This paper contains the results of determinations of the electromotive force of sixteen of the nineteen alloys alluded to in Matthiessen's paper on the conductivity of alloys (*Phil. Trans.*, cl.). The results obtained confirm Matthiessen's conclusion, that only one compound, the tin-gold alloy, exists among the sixteen, which are:—

Bismuth-tin, bismuth-lead, bismuth-gold, bismuth-silver, gold-silver, antimony-lead, cadmium-zinc, antimony-tin, lead-gold, lead-silver, lead-tin, lead-zinc, lead-cadmium, cadmium-tin.

In some cases the addition of a metal to the alloy results in displacement. Thus mercury decomposes the gold-tin compound, and zinc, added to copper-tin alloy, appears to replace the tin.

Discussion.

The President said that owing to the difficulty of obtaining information by purely chemical methods as to the relative affinities of the metallic elements and of the proportions in which they could combine together, observations such as those of Mr. Laurie were of peculiar interest. Apparently the chief difficulty in applying his method was to obtain suitable liquids capable of separately acting on the several alloys. In this respect purely physical methods seemed to be of wider application. Bearing in mind the close relationship of magnesium, zinc, and cadmium, and of copper, silver, and gold, it was especially important to extend the observations made on copper-zinc alloys to all these metals, *i.e.*, to ascertain the behaviour of the several metals of the one group to the several metals of the other, since it may be possible in this way to determine the relative valencies of such metals.

Mr. T. Turner said that Mr. Laurie's experiments on zinc-copper alloys enabled us to correct a mistake in the results obtained by Mallet, and published in his "Construction of Artillery," in which it was stated that the alloy containing 33 per cent of copper was tough and malleable, and that it was used for watch-makers' brass. This statement has been copied into the majority of the text-books, but, as a matter of fact, the 33 per cent alloy corresponds with Laurie's definite compound, and is weak and brittle. Determinations of the electromotive force of tin-copper alloys had also yielded very interesting results, and had led him (Mr. Turner) to the conclusion that the existence of only two definite tin-copper alloys had been proved, the evidence in the case of the third being much less satisfactory. This question he had dealt with in the article "Tin," in Thorpe's Dictionary.

*55. "*A Product of the Action of Nitric Oxide on Sodium Ethylate.*" By G. W. MacDonald, B.Sc., and Orme Masson, M.A., D.Sc.

The authors describe the absorption of nitric oxide by an alcoholic solution of sodium ethylate, the chief product of the action being the sodium salt of an acid,—

$$CH_2N_4O_4H_2.$$

This is a crystalline explosive compound, insoluble in alcohol, but soluble in water. From it are obtained various insoluble metallic salts, the most characteristic one being the sky-blue copper salt, $CH_2N_4O_4Cu$. The properties of some of these salts are described, as also those of the soluble ammonium salt and the unstable acid, obtained in solution by decomposing the copper compound with hydrogen sulphide; and reasons are advanced in support of the hypothesis that the acid is *methylene-dihydroxynitrosamine*, $CH_2[N(NO)OH]_2$.

The sodium salt, obtained by W. Traube, and called by him the sodium salt of methylene-di-isonitramine, $CH_2(N_2O_2H)_2$ (*Ber.*, 1894, 1507), by the action of nitric

oxide on acetone in presence of alcoholic soda, is apparently identical with that now described.

*56. "*The Incomplete Combustion of some Gaseous Carbon Compounds.*" By W. A. BONE, M.Sc., Ph.D., and J. C. CAIN, D.Sc., B.Sc. (Vict.).

The authors have extended the work of Lean and Bone on the explosion of ethylene with less than its own volume of oxygen (*Trans.*, 1892, 873) to mixtures of (1) acetylene, (2) cyanogen and hydrogen, and (3) normal pentane, with an amount of oxygen insufficient to oxidise all the carbon present to monoxide.

The method adopted was to explode the mixtures in a long leaden coil (except in the case of pentane, when a long glass tube could safely be employed), closed by steel taps, having at one end a glass firing-piece, and connected at the other end with a mercury manometer, so that any change in pressure on explosion could be observed. The chemical changes which would occur in such experiments would therefore be those of the "explosion wave." Both the original mixtures and the products were carefully analysed, using a modified form of the McLeod gas-analysis apparatus (see *Phil. Trans.*, 1884, Part 2), which is admirably adapted for accurate work.

On exploding mixtures of acetylene and oxygen at atmospheric pressure, an increase in pressure of about 400 m.m. of mercury was in each case noted. The products contained acetylene, a saturated hydrocarbon (doubtless methane), hydrogen, carbon monoxide, dioxide, and nitrogen.

Analysis shows that when acetylene is exploded with half its volume of oxygen, the resulting interaction may be expressed by the equation $2C_2H_2+O_2=2CO+2C+H_2$.

On exploding a mixture of cyanogen and hydrogen with oxygen a considerable increase in pressure occurred. Carbon was liberated. It appears that practically none of the hydrogen was oxidised during the explosion. The hydrogen and nitrogen actually found agree very well with the assumption that all the oxygen combines with cyanogen to form the monoxide and free nitrogen, whilst the excess of cyanogen breaks up into carbon and nitrogen. The carbon monoxide found is 2 per cent lower than that given by calculation; but it must be remembered that 1½ to 2 per cent of carbon dioxide is formed.

The most interesting point in connection with these experiments is, however, the formation of methane and acetylene. In one case the amounts of both these hydrocarbons were more than 1·7 per cent. The formation of methane and acetylene in these experiments must be due to the direct union of carbon and hydrogen at the high temperature of the explosion wave. Acetylene, it is well known, can be synthesised directly from its elements, but up to the present time methane has not been so obtained. The authors, in an experiment, which, however, they wish to be regarded merely as a preliminary one, satisfied themselves that the synthesis of methane from its elements is not an impossibility. By heating pure sugar-charcoal (which had previously been heated strongly in a current of chlorine, and then in a current of pure hydrogen) contained in a porcelain tube to a white heat in a charcoal furnace, in a current of hydrogen containing a *mere* trace of hydrocarbon impurities, they found that 1·71 per cent (mean of four well-agreeing analyses) of methane was produced. This experiment will be repeated and extended.

The formation of acetylene, together with Berthelot's observation that when acetylene was decomposed by shock (charge of fulminate) only 0·04 per cent of it remained unchanged, incline the authors to the view that the acetylene found is due to reunion of dissociated carbon and hydrogen in or behind the explosion-wave.

A mixture of 1 vol. pentane with 2¼ vols. of oxygen was exploded in a long glass tube. The mixture being just over the "explosion limit," the shock was not very violent, and the flame travelled quite slowly down the tube. carbon was deposited, and an increase in pressure amounting to two atmospheres was observed.

Carbon monoxide, carbon dioxide, acetylene, and hydrogen were produced; the acetylene formed may be accounted for by the fact that carbon and hydrogen were undoubtedly liberated in the explosion at a high temperature.

The experiments now described show that when a hydrocarbon containing n atoms of carbon is burnt with n atoms of oxygen, the interaction may be represented thus:—

$$C_nH_xO_n = nCO + \frac{x}{2}H_2,$$

and that a mixture of cyanogen and hydrogen may be substituted for the hydrocarbon, thus:—

$$C_2N_2+H_2O_2=2CO+H_2+N_2.$$

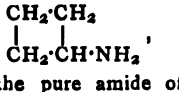
In addition to the various other issues raised by this work, the authors would draw attention to the formation of carbon dioxide in these experiments, as well as in those of Bone and Lean on ethylene, and also to the *amount* of carbon dioxide formed being *less* the *greater* the amount of oxygen (relative to the hydrocarbon) present.

DISCUSSION.

The PRESIDENT, referring to the stress laid by the authors on the production of less carbon dioxide when the greater proportion of oxygen was used, expressed the opinion that probably we were dealing with end results in such cases. It was conceivable that when more oxygen was used, and the temperature was consequently higher at some period during the explosion, the earlier dioxide became unburnt to a greater extent. If the authors were prepared to argue that acetylene was formed during the combustion of acetylene, they must also be prepared to admit that other reversed changes occurred.

57. "*Derivatives of Tetramethylene.*" By W. H. PERKIN, jun., F.R.S.

Contrary to the statement of Freund and Gudeman (*Ber.*, xxi., 2694), a good yield of *tetramethylenamine*,—



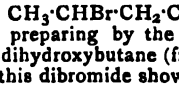
is obtained when the pure amide of tetramethylene-carboxylic acid is attacked with bromine and potash. The base is a colourless pungent-smelling oil, which boils at 81°, and is miscible with water, with evolution of heat; the *hydrochloride*, $C_4H_9N\cdot HCl$, crystallises in long striated needles; the *platinichloride*, $(C_4H_9N)_2\cdot H_2PtCl_6$, crystallises from water in deep orange octahedra.

Hydroxytetramethylene,—

is produced when the hydrochloride of tetramethylene-amine is treated with silver nitrite; it is a colourless oil, which boils at 123°, and possesses an odour similar to that of butyl alcohol. When digested with hydrobromic acid it yields a mixture of *bromotetramethylene*, C_4H_7Br (b. p. 104°), and a *dibromobutane*, which boils at 174°, and which on investigation was found to be identical with 1 : 3-*dibromobutane*, $CH_3\cdot CHBr\cdot CH_2\cdot CH_2Br$, which the author succeeded in preparing by the action of hydrobromic acid on 1 : 3-dihydroxybutane (from aldol).

The formation of this dibromide shows that the tetramethylene ring, like the trimethylene ring, may, under certain conditions, be split by the action of hydrogen bromide, a behaviour of the four-carbon ring which has not before been observed.

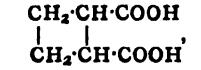
Chlorotetramethylene,



produced by the action of phosphorus pentachloride on

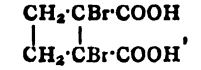
hydroxytetramethylene, is a colourless oil, which boils at 85°, and which, when heated with potassium iodide in alcoholic solution, yields *iodotetramethylene*, C_4H_7I (b. p. 138°), an oil which, like the alkyl iodides, rapidly discolours in the air.

The action of bromine on tetramethylenedicarboxylic acid,—



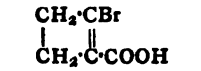
has also been carefully investigated.

When this acid is heated with excess of bromine in the presence of phosphorus, the principal product of the reaction is *dibromotetramethylenedicarboxylic acid*,—

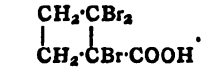


which crystallises in colourless plates, melts at 202—205° with decomposition, and is readily soluble in water; the *methyl salt*, $C_8H_{10}Br_2O_4$, melts at 88—89°, and the *anhydride*, $C_6H_6Br_2O_3$, at 103—104°.

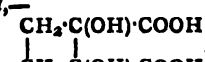
Alkalis, and also potassium iodide, convert dibromotetramethylenedicarboxylic acid into bromodihydrotetrenecarboxylic acid,



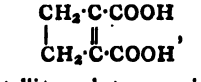
(colourless needles, m. p. 122°), carbon dioxide and hydrogen bromide being eliminated, and this acid, when exposed to bromine vapour, yields tribromotetramethylenecarboxylic acid,—



Silver hydroxide reacts readily with an aqueous solution of dibromotetramethylenedicarboxylic acid, with formation of bromodihydrotetrenecarboxylic acid, and a syrupy acid, which appears to consist of *dihydroxytetramethylenedicarboxylic acid*,—



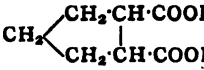
The action of alkalis on methylic dibromotetramethylenedicarboxylate is quite different from that described above in the case of the free acid, the principal product of the reaction being dihydrotetrenedicarboxylic acid,—



a colourless crystalline substance, which melts at 178°, and is not acted on by bromine at ordinary temperatures; at 200° it loses water, with formation of an anhydride.

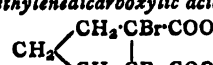
Methylic dihydrotetrenedicarboxylate is formed quantitatively when methylic dibromotetramethylenedicarboxylate is digested in alcoholic solution with potassium iodide; it melts at 46°, and when exposed to bromine vapour is re-converted into the methylic salt of the dibromo acid.

58. "*Pentamethylenedicarboxylic Acid*,—

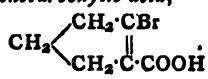


By E. HAWORTH, B.Sc., and W. H. PERKIN, jun., F.R.S.

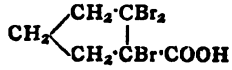
When treated with bromine and phosphorus, pentamethylenedicarboxylic acid behaves very similarly to the corresponding tetramethylene compound (see preceding abstract), the principal product of the reaction being *dibromopentamethylenedicarboxylic acid*,—



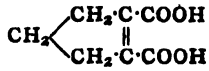
a colourless crystalline substance, which melts at 183—184°, and is readily decomposed by alkalis, forming *bromodihydropentenecarboxylic acid*,—



This acid crystallises in needles, melts at 130° and in contact with bromine vapour is converted into tribromopentamethylenecarboxylic acid,—



Dihydropentenedicarboxylic acid,—



is produced when methylic dibromopentamethylenedicarboxylate is digested in alcoholic solution with potassium iodide, and the product hydrolysed with alcoholic potash; it crystallises from water in colourless prisms, and melts at 178°.

A number of experiments are described in the paper which were instituted with the object of preparing the anhydride of transpentamethylenedicarboxylic acid, a substance which, according to Baeyer's theory of anhydride formation (compare *Trans.*, 1894, 572), should be capable of existence, and ultimately, by digesting the acid for twenty-five minutes with acetic anhydride, and distilling off the excess of the latter under reduced pressure, an oily product was obtained, which on examination was found to consist of the nearly pure anhydride of the trans-acid, and which on distillation was converted quantitatively into the anhydride of the cis-acid.

59. "*Substituted Pimelic Acids.*" By A. W. CROSSLEY, B.Sc., and W. H. PERKIN, jun., F.R.S.

Some time since (*Trans.*, lix., 818) one of us, in conjunction with Mr. B. Prentice, described a method for preparing substituted pimelic acids, and it was shown that, by this method, it was only possible to obtain *αα'-disubstituted* pimelic acids containing the same radicles as, for example, dimethyl pimelic acid,—

$$COOH{\cdot}CH(CH_3){\cdot}(CH_2)_3{\cdot}CH(CH_3){\cdot}COOH;$$

in continuing the study of the pimelic acids various methods have since been tried with the object of preparing monosubstituted pimelic acids and disubstituted pimelic acids of the type—

$$COOH{\cdot}CHR{\cdot}(CH_2)_3{\cdot}CHR'{\cdot}COOH,$$

containing dissimilar radicles.

When trimethylenechlorobromide reacts with the sodium derivative of ethylic ethylmalonate, ethylic ω-chloropropyl ethyl malonate,—

$$(COOC_2H_5)_2{\cdot}C(C_2H_5){\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Cl,$$

is obtained, and this substance when digested, in alcoholic solution, with the sodium derivative of ethylic malonate yields ethylic ethylpentanetetracarboxylate,—

$$(COOC_2H_5)_2{\cdot}C(C_2H_5){\cdot}(CH_2)_3{\cdot}CH(COOC_2H_5)_2,$$

a colourless oil boiling at 275° (75 m.m.). On hydrolysis, this ethereal salt yields a polybasic acid, which at 200° loses carbon dioxide forming ethyl pimelic acid,—

$$COOH{\cdot}CH(C_2H_5){\cdot}(CH_2)_3{\cdot}CH_2{\cdot}COOH,$$

a colourless oil which boils at 260—265° (82 m.m.); the *ethyl salt* boils at 198—200° (82 m.m.); the *amide* is crystalline and melts at 145°.

Ethyl methylpimelic acid,—

$$COOH{\cdot}CH(Me){\cdot}(CH_2)_3{\cdot}CH(Et){\cdot}COOH,$$

was also prepared, by a method which differs somewhat from that described above. The sodium compound of ethylic ethyl malonate was digested in methyl alcoholic solution with chlormethoxypropane,—

$$ClCH_2{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CH_3$$

(*Trans.*, xv., 596), and the resulting methylic methoxypropylethylmalonate,—

$$(COOCH_3)_2{\cdot}C(C_2H_5){\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CH_3,$$

a colourless liquid boiling at 180° (43 m.m.) converted into the acid by hydrolysis.

This acid, on distillation, yields methoxypropanethylacetic acid, $COOH{\cdot}CH{\cdot}(C_2H_5){\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CH_3$, which boils at 250°, and when treated with hydrobromic acid is converted into ω-bromopropylethylacetic acid, $COOH{\cdot}CH(C_2H_5){\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Br$.

The ethereal salt of this acid was then digested with the sodium compound of ethylic methylmalonate; the resulting ethylic ethyl methylpentanetricarboxylate, $CO_2Et{\cdot}CH(C_2H_5){\cdot}(CH_2)_3{\cdot}C(CH_3)(CO_2Et)_2$, a colourless oil which boils at 227—230° (60 m.m.), hydrolysed, and the tricarboxylic acid heated at 200°, until evolution of carbon dioxide has ceased. The residual crude acid, after distillation *in vacuo* after some months, deposited colourless crystals, which repeatedly re-crystallised, melted at about 73°, and consisted of pure ethyl methylpimelic acid; the mother-liquors from these crystals contain a lower melting acid, which is probably a stereoisomeride.

60. "*Homologues of Butanetetracarboxylic Acid, and of Adipic Acid.*" By BEVAN LEAN, D.Sc., B.A., Bishop Berkeley Fellow of Owens College.

When acted on with sodium ethylate, ethyl butanetetracarboxylate forms a disodium derivative, which reacts readily with the iodides or chlorides of the alcohol radicles. A detailed study has been made of the dimethyl-, diethyl-, dicetyl-, and dibenzyl-derivatives so obtained.

These derivatives on hydrolysis yield tetracarboxylic acids, of the general formula—

$$\begin{matrix}HOOC\\HOOC\end{matrix}\!\!>\!CR{\cdot}CH_2{\cdot}CH_2{\cdot}CR\!<\!\begin{matrix}COOH\\COOH\end{matrix}$$

possessing some remarkable properties, which appear not to have been observed in the case of any other organic acids. These acids, although they contain four carboxyl groups, do not in all cases behave as tetrabasic acids. On determining their basicity by titration with potassium hydrate solution, some of them act as dibasic acids; notably is this the case with dibenzylbutanetetracarboxylic acid, the result being the same whether phenolphthalein or litmus is used as the indicator. On the other hand, dimethyl-, diethyl-, and dicetyl-butanetetracarboxylic acids give different results, according as phenolphthalein or litmus is employed as the indicator. They appear tetrabasic with phenolphthalein, while lower results are obtained with litmus solution. And, further, whilst the silver and calcium salts of dimethyl- and diethyl-butanetetracarboxylic are found to be tetrabasic, those prepared in the same way from dibenzyl- and dicetylbutanetetracarboxylic are found to be dibasic.

In connection with the apparently anomalous character of these tetracarboxylic acids, evidence is adduced from the work of Thomsen and Massol on the "Heat of Neutralisation of Acids," and of Ostwald, Walker, and others on the "Dissociation Constants of Acids," to show that the affinity of a polybasic acid is a complex function of the affinities of the several groups which it contains, and that the actions of one or more groups cannot be removed without affecting the affinities of the rest; and, in general, that the chemical character of a group of elements within a molecule depends not alone upon itself, but also upon the nature of those in the presence of which it is found.

The disubstituted butanetetracarboxylic acids, when heated at 200—210°, readily lose two molecules of carbonic anhydride, yielding disubstituted adipic acids, which invariably exist in two modifications, differing usually from one another in a marked manner in melting-point, solubility, and other physical properties; for instance, dimethyladipic acids melt at 70—72° and 142°, diethyladipic acids melt at 51—53° and 136°, dibenzyladipic acids melt at 152° and 211—213°.

On heating the disubstituted adipic acids in sealed tubes with acetyl chloride, in no case was an anhydride obtained, but in view of the recent work of Manasse and Rupe (*Ber.*, xxvii., 1818) on β-methyladipic acid it is possible that sufficient precautions were not taken to prevent the access of moisture from the air. Whilst, however, no anhydride was obtained, it was found that whether the higher melting or lower melting modification was employed, a partial conversion of the one into the other was effected, so that the product consisted of a mixture of the two.

61. "*Contributions to the Chemistry of Cellulose. I. Cellulose Sulphuric Acid and the Products of its Hydrolysis.*" By A. L. STERN, D.Sc.

When cotton cellulose is added to strong sulphuric acid, it dissolves; if the solution be diluted, neutralised with baryta, and filtered, a solution of barium cellulose disulphate is obtained. The free acid, $C_6H_8O_3(SO_4H)_2$, may be obtained by removing the barium by sulphuric acid; it is very unstable, and almost impossible to isolate. The barium salt may be obtained by concentrating its aqueous solution and adding alcohol, when it is thrown down as a syrupy precipitate, which may be dried by first dehydrating with strong alcohol, then exposing in a vacuum over sulphuric acid, and finally heating in a current of dry air at 190° until it ceases to lose weight. Thus obtained, it is a white or slightly coloured glassy powder, very hygroscopic, soluble in all proportions in water, and precipitated from strong solutions by alcohol.

When an aqueous solution of cellulose disulphuric acid is boiled with dilute sulphuric acid, it is hydrolysed. This reaction takes place in two stages, which are, however, not sharply marked off from one another. In the first stage, sulphuric acid is eliminated, and the disulphuric acid is gradually converted into cellulose monosulphuric acid, $C_6H_9O_4{\cdot}SO_4H$, no other product being formed. In the second stage, cellulosic acids containing less sulphuric acid are formed, and also dextrose. The analytical results indicate the presence of only two of these acids, *i.e.*, $C_{12}H_{19}O_9{\cdot}SO_4H$ and $H{\cdot}C_{12}H_{18}O_9{\cdot}SO_4H$.

By no method of fractional precipitation was it possible to obtain any one of the barium salts of these acids in a state of purity, although, when working with them, it was evident that their solubility in dilute alcohol differed. As the purified compounds contained molecular proportions of these salts, it was evident that they combine together. It was also frequently observed that the sugar combined with some of the salts, and thus explained the unsuccessful attempts to obtain it in a crystallisable condition. It was, however, undoubtedly dextrose,

The barium salts and free acids are all readily diffusible, and, when examined by Raoult's method, they give indications of a low molecular weight.

62. "*The Chlorination of Aniline.*" By J. J. SUDBOROUGH, Ph.D.

The author finds that when chlorine is passed into a solution of aniline in chloroform to saturation, parachlor-, 2.4-dichlor-, and 2.4.6-trichloraniline are formed.

The preparation and properties of 2.4.6-trichlorbenzoic acid and 2.4.6-trichlorbenzoyl chloride are also described. The former crystallises from boiling water in long prismatic needles, which melt at 160°. The acid chloride is an oil, which boils at 257° and is remarkably stable towards both boiling water and alcohol.

63. "*Condensation of Benzil with Ethyl Malonate.*" By FRANCIS R. JAPP, F.R.S., and W. B. DAVIDSON, M.A., B.Sc.

By the condensing action of sodium ethoxide on a mixture of benzil and ethyl malonate, the authors have obtained two compounds: (1) the monethyl ester of benzoïnylmalonic acid,—

$$C_6H_5\cdot C(OH)\cdot CH<\begin{matrix}COOC_2H_5\\COOH\end{matrix},$$
$$\quad\quad\quad

the design of the needle, so that, for a given potential-difference, the turning moment divided by the moment of inertia may be as great as possible. The whole instrument is protected from external inductive influence by having the inner surface of its glass case coated with a transparent conducting varnish, which Prof. Ayrton has described elsewhere.

Prof. Ayrton also showed an idiostatic electrometer, whose needle, instead of being suspended, was pivoted on an axle. The instrument is rapid and nearly dead beat in action, and gives a scale-reading of about 3 inches for an E.M.F. of 100 volts.

Prof. S. P. Thompson expressed great admiration for the instruments exhibited, but denied that the law which they served to prove was Ohm's law at all; and this led to some discussion as to what Ohm's law really is.

Prof. Ayrton briefly replied.

CORRESPONDENCE.

HEATING POWER OF SMOKE.

To the Editor of the Chemical News.

Sir,—In the Chemical News, lxx., 248, of last week I have observed a criticism, by Mr. W. A. Dixon, of my paper on the above subject, which appeared in the Chem. News, lxx., 51. Mr. Dixon takes it for granted that I am quite ignorant of the fact that the loss of heat, when fuel is burnt, is due mainly to other causes than the unconsumed carbonaceous matters passing off in the furnace gases, and also makes the amusing statement that in this I am simply one of the great majority of people who are in similar darkness. If Mr. Dixon had taken the trouble to understand my paper, he would have noticed that in my calculations I adopted Playfair's formula for calculating the *practical* heating power of fuel, and did not take that given by the calorimeter, so that the text-book knowledge imparted by him in the first paragraph of his criticism was assumed by me to be too well known to require statement.

I am quite in agreement with Mr. Dixon that the production of smoke is objectionable, but I fail to see what this has to do with my paper, which was written with the purpose of showing that there was practically no *fuel* in smoke, and not at all with reference to loss of *heat* in furnace gases, which is a totally different question.—I am, &c.,

R. R. Tatlock.

City Analyst's Laboratory,
156, Bath Street, Glasgow,
November 27, 1894.

Reaction for Detecting the Presence of Free Sulphur.—José Caraves Gil.—Concentrated alcohol (*e.g.*, 96 per cent) is placed in a flask and heated, with the addition of fragments of glass to prevent bumping. After the vapours of alcohol have expelled the chief part of the air, there is added, drop by drop, a weak solution of potassium polysulphide, and the liquid gradually assumes a colour ranging from light sky-blue to a strong greenish blue. The polysulphides of sodium, ammonium, and calcium possess the same property. Alkaline monosulphides do not colour the liquid, but if a fragment of sulphur is added the colour appears. An excess of caustic alkali decolourises alcohol which has been coloured by polysulphides by forming a monosulphide. Selenides, tellurides, and zinc, cadmium, lead, and arsenic sulphides do not colour the alcohol. With the precipitate obtained by the action of sulphuretted hydrogen upon the arseniates, the reaction of sulphur appears. Alcohol is coloured by carbon disulphide holding sulphur in solution.—*Zeit. Anal. Chemie*, xxxiii., Part I.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxix., No. 20, November 12, 1894.

Researches on the Condensation of the Gases of Electrolysis by Porous Substances, and especially by Metals of the Platinum Group. Applications to the Gas Battery. Accumulators under Pressure.—L. Cailletet and E. Collardeau.—At the close of this memoir M. Berthelot remarked that platinum, palladium, and analogous metals form in the cold true definite combinations with hydrogen and oxygen, especially with the former. Platinum forms two successive hydrides, one of them stable at 200°, but the other dissociable in the cold. The formation of the latter is especially affected by pressure. These are true chemical compounds, and not gases condensed or occluded, as it has been sometimes supposed.

Determination of the Molecular Weight of Liquids.—Ph. A. Guye.—The results of the author's determinations are given in the form of two tables. The molecular weights of the hydrocarbides previously studied by Altschal are the same in the liquid state at the critical point and in the gaseous condition. Ramsay and Shields, who applied their ingenious method to benzene and octane, arrived at the same conclusions for these two hydrocarbons, at least as far as the liquid and gaseous states are concerned.

On Active Amylacetic Acid and some of its Derivatives.—Ida Welt.—The compounds studied are the ethylic ether of amylacetylacetic acid, amylacetic acid, the methylic and ethylic ethers of amylacetic acid; methylhexylacetone and the secondary alcohol methylhexyl carbinol. The principal results of these experiments relate to the ethers of amylacetic acid. If we calculate the values of the product of the asymmetry of the methylic and ethylic ethers we find decreasing numbers; it is the same with the rotatory power. We cannot find in this series an ether with a maximum rotatory power; the first term is already on the descending branch of the curve.

On the Campholenes and the Constitution of Camphor.—A. Béhal.—This paper does not admit of useful abstraction.

Researches on the Oxidation of Alcohols by Fehling's Liquors.—Fernand Gaud.—The author's experiments have been made in two series with an excess of alcohol and with an excess of the reagent. In the former series the ethylic alcohol yielded unchanged alcohol, aldehyd, and acetic acid as a potassium salt. With methylic alcohol in excess the product contained formic aldehyd and potassium formiate. With propylic alcohol the products are propionic aldehyd and potassium propionate. With an excess of the reagent ethylic alcohol yielded potassium acetate and a little copper acetate, but no free aldehyd. With methylic alcohol an excess of Fehling's liquid yielded formic acid and copper formiate. Propylic alcohol yielded potassium propionate and an acid which seemed to be the lactic.

Revue Universelle des Mines et de la Metallurgie. Vol. xxviii., No. 1.

The Explosion at the Albion Mine.—Victor Watteyne.—A translation of the Report of Mr. H. B. Dixon.

On the Total Carbon in Cast Metal for Moulding.—P. Tabay.—The carbon found in different sections of a casting has been found to vary from the bottom to the top

as 3·179 to 3·659, and in other samples as 3·294 to 3·686, and 3·136 to 3·542.

Determination of Sulphur in Pyrites.—F. Johnson.—(From the CHEMICAL NEWS).

Popular Method for the Determination of Carbonic Anhydride in Air.—(From the CHEMICAL NEWS).

Bulletin de la Société Chimique de Paris.
Series 3, Vols. xi.-xii., Nos. 18 and 19.

This number presents a portrait and a biography of Professor G. Salet. The deceased, born in 1844, had at an early age come in friendly contact with Boussingault, and afterwards became the pupil and ultimately the successor of Würtz. His favourite study was spectroscopy, on which subject he contributed thirteen papers to the *Comptes Rendus*, as well as some others published in the *Bull. de la Soc. Chim.* and the *Annales de Chimie et Physique*. He studied the cause of the movements of the radiometer, and verified and interpreted the law of Stokes. It is remarkable, but significant, that his physico-chemical studies prevented him from being elected as a Member of the Academy of Sciences. His name was on the list of candidates when someone made the rather pedantical discovery that he was too much a physicist for the Chemical Section, and too much of a chemist for the Physical Section! His regretted death in the early part of this year, at the age of 50, gave no opportunity for this eccentric decision to be rescinded. His principal work is the "Traité Elementaire de Spectroscopie" (Masson, 1888). He also edited the *Agenda du Chimiste* from 1877 to 1894. As an earnest and successful cultivator of the border-land between chemistry and physics, his premature death is gravely to be lamented.

A New Rectifying Apparatus, with Analysers and Retrograding Plates.—Ernest Barillot.—This memoir cannot be made intelligible without the complicated figure.

Thermic Study of Calcium Oxybromide and Oxyiodide.—M. Tasilly.—A thermo-chemical paper not adapted for useful abstraction.

On Propylpropylidene-Amine.—F. Chancel.—This base is a colourless mobile liquid of an offensive ammoniacal odour, boiling at 102° under a pressure of 760; its specific gravity at 0° is 0·84. It is sparingly soluble in water, and turns litmus paper blue. It contains 14·43 per cent of nitrogen.

On the Propylacetylacetamides.—F. Chancel.—An account of monopropylacetamide and dipropylacetamide. The former compound is a slightly syrupy liquid, of a slight odour, miscible in water, but sparingly soluble in saline solutions. The second compound is very similar in its properties.

On Tetrapropylurea.—F. Chancel.—This compound is slightly syrupy, of an aromatic odour resembling that of mint, and of a burning taste. It boils without decomposition at 258° under pressure of 755 m.m. At 0° its specific gravity is 0·905.

The Gresham University.—This projected University, after having received Parliamentary sanction, has collapsed from an unexpected difficulty. King's College was of course to form an essential part of the new institution, but under its statutes it imposes a religious test on its professors and students. This arrangement is incompatible with the regulations of the proposed University, and it seems that neither side can or will give way. A long and warm discussion was held at King's College, but led to no result. Hence, pending the elaboration of some *modus vivendi*, the Gresham University is at a standstill.

MEETINGS FOR THE WEEK.

MONDAY, Dec. 3rd.—Royal Institution, 5. General Monthly Meeting.
—— Society of Chemical Industry, 8. (At Burlington House). "The Rational Sterilisation of Alimentary Liquids," by E. W. Kuhn. "An Investigation of the Natural Sodium Sulphate Lakes of Wyoming, U.S.A.," by Dr. D. H. Attfield, M.A. "Specimens of India-rubber, and Petroleum Oil, Varnish, and Soap," Exhibited by Thos. Christy, F.L.S.
—— Society of Arts, 8. (Cantor Lectures. "Modern Developments in Explosives," by Prof. Vivian B. Lewes.
TUESDAY, 4th.—Institute of Civil Engineers, 8.
—— Pathological, 8.30.
WEDNESDAY, 5th.—Society of Arts, 8. "Fire Protection," by Edwin O. Sachs.
—— Geological, 8.
THURSDAY, 6th.—Royal, 4.30.
—— Royal Society Club, 6.30.
—— Society of Arts, 4.30. "Roman and British Indian Systems of Government," by the Hon. W. Lee-Warner.
—— Chemical, 8. Ballot for the Election of Fellows. "The Use of the Globe in the Study of Crystallography," by J. Y. Buchanan, F.R.S. "Latent Heat of Fusion," by H. Crompton. "New Method of Preparing Dihydroxytartaric Acid," by H. J. H. Fenton. "Essential Oil of Hops," by A. C. Chapman.
FRIDAY, 7th.—Geologists' Association, 8.
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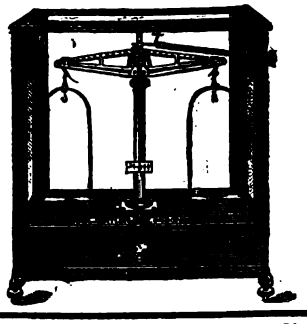

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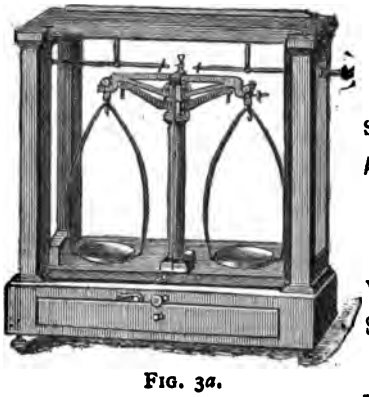

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ATOMIC VOLUMES.

By C. T. BLANSHARD, M.A.

Since Prof. Lothar Meyer's work on atomic volumes there have been no tables of these important physical properties constructed, to harmonise with the most recent or best authenticated values for both atomic weight and specific gravity. I subjoin a Table so constructed for the elements, placing the hitherto received values, according to Lothar Meyer, in the last column. O = 16. The specific gravity is taken at 0° C.

From these Tables the following laws can be deduced:—

1. In the *metallic* groups, I. and II., the atomic volumes vary most.
2. In the *intermediate* groups, III. and IV., and the *a* groups, the atomic volumes vary but little.
3. In the *non-metallic* groups, V., VI., and VII., and the *b* groups, the atomic volumes vary least, approaching a constant for each group.

Group.	Element.	W.	D.	$\frac{W}{D}$	Old value.	Authorities.
I.	Lithium	7·03	0·59	11·9	12	Stas; Bunsen.
	Sodium	23·05	0·97	23·8	24	Stas; Gay-Lussac and Thénard.
	Potassium	39·136	0·87	44·9	45	Stas; Gay-Lussac and Thénard.
	Rubidium	85·48	1·52	56·4	56	Godeffroy; Bunsen.
	Cæsium	132·99	1·88	70·7	70	Bunsen; Setterberg.
I.*a*.	Copper	63·604	8·94	7·0	8	Richards; various.
	Silver	107·93	10·53	10·25	10	Stas; Rose.
	Gold	197·16	19·33	10·20	10	Krüss; Rose.
II.	Beryllium	9·1	1·85	4·9	6	Nilson and Pettersson; Humpidge.
	Magnesium	24·287	1·74	13·9	14	Burton and Vorce; Bunsen.
	Calcium	40·00	1·57	25·6	25	Erdmann and Marchand; Matthiessen.
II.	Strontium	87·6	2·54	33·9	34	Dumas; Matthiessen.
	Barium	137·0	3·75	36·5	36	Dumas; Kern.
II.*a*.	Zinc	65·34	7·10	9·2	10	Gladstone and Hibbert; Rammelsberg.
	Cadmium	111·802	8·55	13·0	13	Partridge, Clarke; Schröder.
	Mercury	200·36	13·596	14·7	14	Erdmann and Marchand; Regnault.
II.*b*.	Iron	56·00	7·86	7·1	7	Erdmann and Marchand; various.
	Ruthenium	101·66	12·63	8·05	8	Joly.
	Osmium	191·18	22·48	8·50	8	Seubert; Deville, Joly, and Vezes.
III.	Boron	10·825	2·5?	4·13	4	Abrahall; Hampe.
	Aluminium	27·08	2·6	10·4	11	Mallet; Deville, Heeren.
	Scandium	44·09	?	?	?	Nilson.
	Yttrium	89·02	?	?	?	Cleve.
	Lanthanum	138·2	6·1	22·6	22	Bettendorff, Brauner; Hillebrand and Norton.
	(The Boron contains a trace of aluminium).					
III.*a*.	Gallium	69·9	5·95	11·8	12	Boisbaudran.
	Indium	113·68	7·42	15·3	14	Bunsen; Winkler.
	Thallium	204·146	11·85	17·2	17	Crookes; De la Rive.
IV.	Carbon (ad.)	12·003	3·518	3·41	3	Roscoe; v. Baumhauer.
	Silicon (ad.)	28·4	2·39	11·8	11	Thorpe and Young; Winkler.
	Titanium	48·13	?	?	?	Thorpe.
	Zirconium	90 63	4·15?	21·8?	21	Bailey; Troost.
	Cerium	140·22	6·65	21·09	21	Brauner; Hillebrand and Norton.
	Thorium	232·4	11·0	21·13	?	Nilson and Krüss.
IV.*a*.	Germanium	72·32	5·469	13·2	?	Winkler.
	Tin	118·08	7·29	16·2	16	Van der Plaats; Matthiessen.
	Lead	206·9	11·352	18·2	18	Stas; Reich.
IV.*b*.	Cobalt	58·89	8·6?	6·89	6	Zimmermann; Rammelsberg.
	Rhodium	102·96	12·1?	8·50	8	Seubert and Kobbé; Deville and Debray.
	Iridium	193·18	22·42	8·97	8	Seubert, Joly; Deville and Debray.
V.	Nitrogen	14·041	0·90	15·6	?	Stas; Wroblewski.
	Phosphorus (red)	31·025	2·2	14·1	13	Schrötter; Hittorf.
	Arsenic (am.)	74·97	4·71	15·9	13	Dumas; Bettendorff.
	Antimony	119·96	6·697	17·9	18	Cooke; Schröder.
	Bismuth	208·6	9·75	21·4	21	Marignac; Classen, Schröder.
	(The value of D for liquid nitrogen is probably too low; if taken as $\frac{1}{14}$, that of oxygen—and the boiling-points are almost the same—it becomes 0·98, giving a concordant atomic volume of 14·3).					

Group.	Element.	W.	D.	$\frac{W}{D}$	Old value.	Authorities.
V.*a.*	Vanadium	51·21	5·5	9·31	9	Roscoe.
	Niobium	94·20	7·06	13·3	14	Marignac; Roscoe.
	Tantalum	182·8	10·4	17·6	16	Marignac; Roscoe.
VI.	Oxygen	16	1·12	14·3	?	Berzelius; Olszewski.
	Sulphur (rhom.)..	32·0626	2·075	15·45	15	Stas; Pisati.
	Selenium (cryst.)	79·070	4·5	17·57	17	Pettersson and Eckmann; Rammelsberg.
	Tellurium (cryst.)	124·85	6·246	19·99	20	Brauner; Priwosnik.
VI.*a.*	Chromium	52·14	6·73	7·45	8	Rawson, Meinecke; Glatzel.
	Molybdenum ..	96·08	8·6?	11·17?	11	L. Meyer; Debray.
	Uranium	239·4	18·7	12·79	13	Zimmermann.
VI.*b.*	Nickel	58·1	8·9	6·53	6	Krüss and Schmidt; Schröder.
	Palladium	106·56	12·148	8·77	9	Keiser; Lowry.
	Platinum	194·83	21·5	9·06	9	Seubert; Deville and Debray.
VI.*c.*	Erbium	166	?	?		Cleve.
	Tungsten	184·08	18·77	9·83	10	Roscoe, Waddell; Waddell.
VII.	Fluorine	19·01	?	?		Dumas, Christensen, Moissan.
	Chlorine	35·45	1·46	24·3	25	Stas; Knietsch.
	Bromine	79·96	3·187	25·0	26	Stas; Pierre, Quincke, Van der Plaats.
	Iodine	126·86	4·95	25·6	25	Stas, Cooke; Gay-Lussac.
VII.*a.*	Manganese.. ..	55·1	7·39	7·45	6	Dewar and Scott, Marignac; Glatzel.

PROTEIDS OF THE KIDNEY BEAN.

By THOMAS B. OSBORNE.

The Kidney bean (*Phaseolus vulgaris*, variety "White Medium Field Bean") contains three proteids, viz., two globulins and a proteose. The last-named is present in very small proportion and has not been obtained pure in quantity sufficient for analysis.

The two globulins are both very soluble in dilute saline solutions, from which they are precipitated by acids, the precipitates being soluble in common-salt solution. By prolonged dialysis of their solutions they separate out and thereby become partially insoluble in brine.

Phaseolin.—This name is now first applied to the proteid most abundant in the kidney bean. It probably forms about 20 per cent of the air-dry seed. Pure water dissolves it from the ground bean (with help of the salts present) to the extent of about 11 per cent, and 2 per cent sodium chloride solution readily extracts about 15 per cent. It dissolves in $\frac{1}{10}$ per cent potash solution and separates unaltered on neutralisation.

Phaseolin is insoluble in cold or hot water. Hydrochloric acid precipitates it from its solution in 1 per cent sodium chloride brine, but not from its solution in 10 per cent brine, when added either in small or large quantity. From 10 per cent sodium chloride brine containing much of this proteid it is precipitated by diluting with much water. Its brine solutions are precipitated slightly by saturating with sodium chloride or magnesium sulphate and completely by excess of ammonium sulphate.

Solution of phaseolin in 10 per cent sodium chloride brine, heated to 95° C., becomes turbid, and prolonged heating to 100° produces a slight flocculent separation. From hot concentrated solutions in brine it separates out partially on cooling and may then appear as spheroids. By dialysis in alcohol it has been obtained in tetrahedral crystals.

Phaseolin has a composition—as may be seen from the subjoined figures—nearly like that of oat-myosin. Ritthausen, in 1884, found as the average of three analyses nearly the same composition as that obtained by the writer, whose results, here given, are the mean of twenty-four more or less complete and fairly accordant analyses, made on as many distinct preparations.

Phaseolin differs from oat-myosin in containing less sulphur, in not separating from 10 per cent salt solution by adding acids or salt, and in being much less readily thrown down therefrom by dilution or dialysis.

	Phaseolin. Ritthausen.	Phaseolin. Osborne.	Oat-Myosin. Osborne.	Phaselin. Osborne.
Carbon ..	52·55	52·58	52·34	51·60
Hydrogen..	7·09	6·84	7·21	7·02
Nitrogen ..	16 18	16·47	16·88	14·65
Sulphur ..	0·43	0·56	0·88	0·49
Oxygen ..	23·75	23·55	22·69	26·24
	100·00	100·00	100·00	100·00

Phaselin is the name proposed for the less abundant globulin of the kidney bean, which appears to constitute about 2 per cent of the air-dry seed. As shown by the foregoing average of the fairly agreeing analyses of eleven preparations, this substance has a very low nitrogen and high oxygen content.

Phaselin is very soluble in highly dilute saline solutions, and remains dissolved in them after phaseolin has been separated by dialysis. It is slowly coagulated by heat at temperatures varying with the amount of salts present and the rapidity of heating. Its solution in 10 per cent sodium chloride brine becomes turbid at 52°—55° and flocks form at 68°—70°. Aqueous extracts of the meal become turbid at 60° and scarcely more so at 100°. Aqueous extracts to which 10 per cent of sodium chloride has been added, appear turbid at 37° and flocky at 52°. Complete coagulation requires long-continued heating at the higher temperatures.—*Report of Conn. Exp. Station.*

Physiological Action of Tellurium, Tungsten, Cerium, and Thorium.—Dr. K. Bokorny gives in the *Chemiker Zeitung* an account of his experiments on the physiological action of the above substances. Free telluric acid and the alkaline tellurates may be considered as harmless for the lower plants and animals. The tungstates if poisonous are so in a very slight degree only. This is the more important as uranium, the metal standing next in the series, is decidedly a poison; 0·5 to 2 m.grm. of uranium-sodium tartrate per kilo. of the weight of the body kill animals with paralytic symptoms. Cerium is slightly poisonous, but less so than lead. Thorium is not poisonous.

ON THE

MICROBES INVOLVED IN THE ENSILAGE OF GREEN FODDER;

AND ON

THE VARIATIONS OF SUGAR AND ACIDITY WITH TEMPERATURE AND TIME.

By A. B. GRIFFITHS, Ph.D., F.R.S.E., &c.,
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Two varieties, known as acid and sweet silage, are produced by the several methods of carrying out the process for the conversion of green fodder into silage. Whether acid or sweet silage results from the process is determined chiefly by the temperature at which fermentation takes place within the mass of herbage; and the silage is acid or sweet according to the presence or absence of certain acids belonging to the fatty series.

If an open-air silage stack is viewed in section, from top to bottom, the lower layers will be seen to be greener than the upper—the colour becoming brownish green towards the top. The bottom layers have been converted into acid silage, because the pressure of the mass of herbage above has excluded atmospheric oxygen, and fermentation has taken place at a low temperature. As less weight was applied to the upper layers, there was freer access of atmospheric oxygen, and consequently a higher temperature was produced.

If the fermentation proceeds at a temperature below 49° C., acid silage is the result; and if the fermentation has not risen above 32° C., low-temperature acid silage is produced. In low-temperature acid silage the principal microbe isolated was the *Bacterium aceti*, or the acetic acid ferment.

Between the temperatures of 32° C. and 49° C., high-temperature acid silage is produced; and the microbes which are active in the production of this kind of fermentation are the *Bacterium lactis* (the lactic acid ferment), *Bacterium aceti*, *Bacillus butyricus* (the butyric acid ferment), and *Bacillus subtilis*.

If the fermentation of the green fodder proceeds between the temperatures of 49° C. and 55° C., there are generally layers of sweet and acid silage intermingled. The microbes isolated from silage produced between these temperatures were the *Bacterium lactis*, *Bacillus butyricus*, and some new species to be described later in this paper.

If the fermentation of the fodder proceeds between the temperatures of 60° C. and 70° C., sweet silage is the result. Between these temperatures the *Bacterium aceti*, *Bacterium lactis*, *Bacillus butyricus*, and *Bacillus subtilis* are killed or become inactive, but at temperatures between 52° C. and 68° C. two new species of bacilli make their appearance during the process of making sweet silage.

All the microbes previously mentioned have been isolated, from the different silages produced at the temperatures mentioned by the following processes:—Many samples were taken of each variety of silage, and they were separately examined. Each sample was shaken up with sterilised water, and this fluid was used for inoculating purposes.

I.—*Silage produced at a Temperature below 32° C.*

Twenty tubes, each containing sterilised ethyl alcohol (6 per cent), were inoculated with the fluid derived from samples of silage produced at a temperature below 32° C. In seventeen of the tubes *Bacterium aceti* was developed in abundance, and acetic acid produced. First, second, and third attenuations were obtained from these cultivations.

Twenty tubes, each containing a sterilised solution of lactose, were inoculated with the same fluid, but in only three tubes did *Bacterium lactis* make its appearance. After inoculation sterilised oil was poured over the surface of the solution in each tube, the object being to keep out air, as *Bacterium lactis* is an anaërobic microbe.

The only other microbes isolated by the methods of plate cultivation, and fractional cultivation, were the *Bacillus butyricus* and *Bacillus subtilis*. These microbes are only present in small numbers in silage made at a temperature below 32° C.

The following are the analyses* of two different kinds of acid silage produced by low fermentation at a temperature below 32° C.:—

	From immature fodder.	From fodder just in bloom.
Water	75·00	74·41
Albumenoids	1·53	1·82
Sugar and other soluble carbohydrates	2·31	2·81
Woody fibre	19·63	19·71
Ash	1·33	1·25
	100·00	100·00
(*a*) Volatile acids, chiefly acetic acid, but containing traces of formic and butyric acids	1·56%	0·62%
(*b*) Non-volatile acids, chiefly lactic acid	0·10%	0·09%

From these results it will be seen that at a temperature below 32° C. acid silage is the result; the acidity being produced chiefly through the action of *Bacterium aceti*, or the acetic acid ferment. A small quantity of lactic acid is also produced. If the fodder is immature at the time it is ensiled, the degree of acidity is greatly increased. The right time for ensiling grass is when the majority of the plants are in bloom; clover, when the whole crop is in flower; peas and vetches, when the pods are forming, but before they commence filling; and oats and other cereals should be ensiled when the grain commences to form. These remarks concerning the right time for ensiling also apply to all temperatures at which green fodder is converted into silage.

II.—*Silage produced at Temperatures between 32° and 49° C.*

Twenty tubes, each containing a sterilised solution of lactose, were inoculated with the aqueous fluid derived from samples of this kind of silage. After inoculation, sterilised oil was poured over the surface of the solution in each tube, and the tubes were then placed in an incubator kept at about 36° C. In eighteen of the tubes *Bacterium lactis* was developed in great abundance, and lactic acid was demonstrated to be present in the tubes by applying the usual chemical tests.

Twenty tubes, each containing sterilised ethyl alcohol (6 per cent), were inoculated with the fluid derived from the same samples of silage. In eight of the tubes *Bacterium aceti* developed; the morphological characters of the microbe were determined, and the presence of acetic acid was proved by the usual chemical tests.

By means of the method of plate cultivation on nutrient gelatin, the aqueous fluid from the same samples of silage yielded rounded white colonies (with radiating processes) of the *Bacillus subtilis*. Steamed potatoes and agar-agar were inoculated with the colonies produced on nutrient gelatin. In each case a cream-coloured layer was formed, which ultimately became granular and dry. In the deeper layer of the nutrient gelatin (*i.e.*, of the above-mentioned gelatin plates) yellow or brownish colonies of a granular appearance were produced, and the gelatin was liquefied. On inoculating agar-agar with a portion of these yellow colonies, a viscid yellow layer was formed. When a sterilised solution of starch and calcium lactate was inoculated with the same colonies, butyric acid fermentation proceeded rapidly. The butyric acid was proved by

* Average of six analyses in each case.

the usual chemical tests. Consequently the yellow colonies were due to the growth of the *Bacillus butyricus*.

The following are the results of the analyses* of two different kinds of acid silage produced by fermentation at temperatures between 32° and 49° C.:—

	From immature fodder.	From fodder just in bloom.
Water	73·00	70·24
Albumenoids	1·69	2·21
Sugar and other soluble carbohydrates	2·00	2·93
Woody fibre	22·33	22·61
Ash	1·98	2·01
	100·00	100·00
(*a*) Volatile acids (acetic and butyric acids) ..	1·19%	0·38%
(*b*) Non-volatile acids, chiefly lactic acid	0·31%	0·23%

It will be seen that at temperatures between 32° and 49° C., acid silage is the result; but between these temperatures the lactic acid fermentation becomes more marked; which is proved by the increased percentage of lactic acid in the silage. If the fodder is immature at the time it is ensiled, the degree of acidity is increased.

III.—*Silage produced at Temperatures between 56° and 70° C.*

Twenty tubes, each containing sterilised ethyl alcohol (6 per cent), were inoculated with the fluid derived from samples of silage produced at temperatures between 56° and 70° C. *Bacterium aceti* did not develop in any of the tubes.

Twenty tubes, each containing a sterilised solution of lactose, were inoculated with the same fluid, but in none of the tubes did *Bacterium lactis* make its appearance.

Bacillus butyricus and *Bacillus subtilis* were also absent, as proved by plate cultivation and fractional cultivation. Hence, it appears that when green fodder is converted into silage at temperatures between 60° and 70° C., the acid ferments are destroyed, or they are rendered so inactive as to be incapable of performing their own specific fermentations when incubated at the most suitable temperatures for their proper development and growth.

By means of fractional cultivation two new species of bacilli have been isolated from silage made at temperatures between 52° and 68° C. Many samples of this silage were shaken with sterilised water, and the fluids were then mixed together. The mixed fluid was used in the study of the microbes present therein.

Fifty tubes containing sterilised bouillon (beef), with a small quantity of sugar added, were each inoculated with the fluid derived from samples of silage produced at temperatures between 60° and 70° C. They were then placed in incubators for three days at temperatures varying between 50° and 70° C. In ten tubes kept at 56° C a new microbe (which we will term *x*) was developed. Sub-cultures were prepared, but in all only the microbe *x* was isolated. Ten tubes were kept at 65° C., and in eight of them there developed another microbe (which we will term *z*). Ten tubes were kept at 68°—70° C., and in three of them there developed the microbe *z*. Ten tubes were kept at 58°—66° C., in five of the tubes there developed the microbe *x*, in two of the tubes there developed the microbe *z*, and three tubes remained sterile. Eight tubes were kept at 50°—52° C., in three of the tubes there developed the microbe *x*, and five tubes remained sterile. Eight tubes were kept at 70°—74° C., but both remained sterile.

In all the above cases sub-cultures were obtained, and thereby pure cultures obtained of the two microbes *x* and *z*. No other microbes were isolated; consequently *x* and *z* appear to be active agents in producing the characteristic odour of sweet silage.

The microbe *x* grows between the temperatures of 50° and 66° C; but it is best cultivated artificially at 56° C.

The microbe *z* grows between the temperatures of 58° and 68° C., but it appears to grow best in artificial media at 65° C.

The Biology of the Two Microbes.

The microbe *x* is a bacillus which measures 4 μ in length and 0·5 μ in breadth, and it produces oval spores. This microbe readily grows in a sterilised decoction of green fodder at 56°C.; and in this medium it gives rise to small quantities of valeric acid $C_5H_{10}O_2$ or $CH_3.C_2H_5$: CH.COOH. Hence the reason that the author proposes to name the microbe *x*, *Bacillus valericus*. The valeric acid was separated, and it answered in every way to ordinary active valeric acid or methylethylacetic acid. When grown in sterilised sugar bouillon, *Bacillus valericus* produces the characteristic odour of valeric acid. This microbe does not flourish on solid media, but in liquid media containing a soluble carbohydrate, and kept at about 56° C, it grows most luxuriantly. In 24 hours after inoculation it gives rise to a turbidity; afterwards the bacillus forms a dense resistant whitish pellicle on the surface of the nourishing medium, and in this copious shore-formation takes place. If shaken the pellicle falls to the bottom of the medium, and soon a new pellicle is formed. This microbe is readily stained with a solution of methyl violet.

The microbe *z* is also a bacillus, and measures from 4 to 7 μ in length, and from 1 to 1·5 μ in breadth. It frequently forms chains and produces oval spores. This microbe grows in a sterilised decoction of green fodder at 65° C., and it gives rise to an agreeable odour resembling some of the esters (ethereal salts); but the substance (or substances) which produces this odour was present in too small a quantity for extraction. Considering the high temperature at which the microbe *z* flourishes the author proposes to name it *Bacillus thermicus*. In liquid media containing a soluble carbohydrate, this microbe gives rise to a whitish, fluffy, or loose growth at the bottom of the tube. It also grows on sterilised solid egg albumin at 65° C., giving rise to yellowish colonies; but on this medium it does not give rise to the odour of the esters. If, however, a subculture is obtained in liquid media containing a soluble carbohydrate the characteristic odour is once more established. *Bacillus valericus* and *Bacillus thermicus* have each the power of converting starch into glucose. This is probably due to the secretion of soluble ferments or enzymes. But these substances have not been isolated. Both of the new microbes have also been isolated from silage produced at temperatures between 49° and 55° C.

The following are the results of the analysis* of sweet silage produced, from green fodder just in bloom, by fermentation at temperatures between 56° and 70° C.:—

Water	73·05
Albumenoids	2·52
Sugar and other soluble carbohydrates ..	4·00
Woody fibre	18·21
Ash	2·22
	100·00
(*a*) Volatile acids, chiefly valeric acid ..	0·06 p.c.
(*b*) Non-volatile acids, calculated as lactic acid	0·02 „

Between the temperatures of 56° and 70° C., *sweet* silage is the result. This silage contains a mere trace of acids, and it contains 4 per cent of sugar. The "fruity" odour of sweet silage is principally due to valeric acid and certain esters.

* Average of four analyses in each case.

* Average of four analyses.

From these investigations the microbes involved in the ensilage of green fodder are the following:—

From acid silage.	From sweet silage.
Bacterium aceti.	*Bacillus valericus.*
,, *lactis.*	,, *thermicus.*
,, *butyricus.*	
,, *subtilis.*	

Sweet silage, on exposure to air, becomes mouldy in a comparatively short time, whilst well-made acid silage may be kept sound for six or more months when freely exposed to air without turning mouldy. Immature green fodder does not keep well when put into silos; and over-ripe stringy green fodder abounding in woody fibre often keeps extremely well when submitted to the process of ensilege, but it never makes good nutritious silage.

AN IODOMETRIC METHOD FOR THE ESTIMATION OF TELLURIC ACID.*

By F. A. GOOCH and J. HOWLAND.

In his valuable and extended study of possible volumetric methods for the estimation of tellurium, Brauner (*Journal of the Chemical Society*, 1891, pp. 58, 238) has investigated the action of iodine upon an alkaline tellurite, and finds that the oxidation is slow and incomplete at ordinary temperatures, while at 100° C. and in presence of a sufficient excess of iodine complete oxidation takes place, though the difficulty of estimating the excess of iodine not directly utilised in the reaction is so great as to render the method practically inapplicable to the determination of tellurium. The difficulty in effecting oxidation in alkaline solution naturally suggests the reversal of the reaction in an attempt to reduce telluric acid by the action of hydriodic acid in acid solution. Upon putting the matter to the test we find the reduction of telluric acid does take place, but we have been unable to prevent its going too far. Thus, on boiling a solution made by adding 10 c.m.^{3} of sulphuric acid of half-strength and 3 grms. of potassium iodide in 90 c.m.^{3} of water containing a little more than 0·1 grm. of telluric acid, the liquid darkened, deposited dark grey crystalline scales, and evolved iodine which, when collected and titrated with sodium thiosulphate, proved to be 20 per cent in excess of the theoretical yield, assuming that the reduction should result in the production of tellurous acid. A similar experiment made in like manner, excepting that the liquid was heated for fifteen minutes in a closed bottle on the water-bath instead of being subjected to boiling, with the idea that the presence of the free iodine might tend to prevent excessive reduction of the tellurium, indicated a yield of free iodine about 6 per cent in excess of what it should be if tellurous acid is the sole product of reduction. In this case the titration of the free iodine was made by sodium thiosulphate in the presence of the reduced tellurous acid, but we found by independent experiment that the determination of free iodine associated with tellurous acid may be accomplished with a fair degree of accuracy provided the solution be cold and dilute, and the final reaction secured by adding the thiosulphate in slight excess and restoring the colour permanently by standard iodine. Even under the most favourable conditions the tellurous acid is somewhat acted upon by sodium thiosulphate, even before the free iodine is entirely bleached, and the reaction in the reverse titration by standard iodine is slow in coming, though finally definite; but if the solution is hot the thiosulphate precipitates tellurium in flocky condition.

The excessive action of the iodide suggested the substitution of potassium bromide—an agent which proved of value in reducing arsenic acid as described in a recent paper from this laboratory—and, the preliminary experimentation proving to be encouraging we set about the preparation of telluric acid of definitely known strength. We weighed out accurately tellurous oxide, prepared by oxidising presumably pure crystallised tellurium with nitric acid and igniting the product at a low red heat, dissolved the weighed oxide in a few c.c. of a strong solution of potassium hydroxide, precipitated the tellurous acid by the careful addition of dilute sulphuric acid, and dissolved the precipitate in 10 c.m.^{3} of sulphuric acid of half-strength. The solution thus obtained was treated with potassium permanganate in excess, the manganic oxide and the excess of permanganate were bleached by oxalic acid added to the hot solution, and the excess of oxalic acid was destroyed by the addition of a dilute solution of the permanganate until the faintest possible blush of colour appeared. For the experiments involving the treatment of the larger amounts of tellurium every preparation was made individually in the manner described; for the experiments with smaller amounts a single preparation was made and the solution thus obtained was diluted to a half litre, and portions of this standard solution were drawn from a burette as occasion required.

The equivalent of the so-called element tellurium is, as Brauner has shown (*Journ. Chem. Soc.*, 1889, 382), so variable with the mode of determining that constant and the preparation of material that we employed a preparation of tullurous oxide which had been tested as to its equivalent weight by Brauner's excellent method of oxidation by potassium permanganate. The results of these tests are recorded in the accompanying table. In series I the alkaline solution of the oxide was diluted to 100 c.m.^{3} and oxidation was effected in it by standard permanganate added in excess. Sulphuric acid of half-strength was added to neutralisation and then 5 c.m.^{3} more, the liquid was heated, a solution of oxalic acid of known value was introduced to an amount slightly in excess of that needed to destroy the manganic oxide and excess of permanganate, and the surplus of oxalic acid was removed by standard permanganate. In series II. the alkaline solution of the oxide was neutralised with dilute sulphuric acid, and 1 c.m.^{3} of sulphuric acid of half-strength was added. The oxidation was accomplished from this point exactly as in series I, the only difference being that it took place in the presence of a slight excess of sulphuric acid instead of in alkaline solution. The permanganate used in both series was standardised ultimately against lead oxalate.

Series I.

TeO_3 taken. Grm.	Oxygen required for oxidation.	Molecular weight of TeO_3 when O=16.	Mean.
0·1200	0·01202	159·7	
0·0783	0·00785	159·6	
0·0931	0·00940	158·7	158·88
0·1100	0·01119	158·	
0·0904	0·00909	159·5	
0·1065	0·01078	157·8	

Series II.

0·0910	0·00935	159·2	
0·0910	0·00910	159·9	
0·0911	0·00924	157·7	
0·0913	0·00915	159·6	159·03
0·0912	0·00915	159·4	
0·0914	0·00923	158·4	

The mean value of these determinations assigns to the tellurous oxide which we employed a molecular weight of about 159, and to the element tellurium an atomic weight of 127, when oxygen is 16. Brauner advocates the application of a correction made necessary by the excessive decomposition of the permanganate in the oxidation; but inasmuch as the oxidation in series I. took place in alkaline solution under conditions in which we have no absolute proof that unused oxygen is liberated to any considerable degree from the permanganate, while in series II.

* Contributions from the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, xxvii., Nov., 1894.

the excess of sulphuric acid was purposely restricted to the lowest limit—the sulphuric acid having been shown in a previous paper from this laboratory (Gooch and Danner, *Am. Jour. Sci.*, xliv., 301) to be the chief agent in inducing the excessive decomposition of the permanganate—we incline, provisionally at least, to accept in this case the result of the analyses without correction.

In the test experiments the telluric acid, prepared in the manner described, was introduced into the apparatus for distillation with 3 grms. of potassium bromide, care being taken to insure in the 50 c.m.³ or more of liquid the presence of 10 c.m.³ of sulphuric acid of half-strength. A current of carbon dioxide was passed through the apparatus, the solution was boiled to set free the bromine which was absorbed in potassium iodide and estimated by standard sodium thiosulphate. In handling the larger amounts of tellurium we found it desirable to make the preparation of the telluric acid in the distilling flask and to boil out the oxygen and ozone set free in the preparation before proceeding with the operation. The apparatus which we used consisted of a Voit's gas-washing flask, with sealed-in inlet tube and ground-in outlet tube, used as the distillation flask, to which was joined by a sealed joint the inlet tube of a Drexel washing bottle to the outlet tube of which was sealed a Will and Varrentrapp absorption apparatus. The washing bottle and attached bulbs contained a solution of 3 grms. of potassium iodide, and the former was kept cool by standing it during the distillation in a vessel of cold water. The absorption of the bromine took place almost entirely in the bottle, only traces of iodine being set free in the bulbs. The results of our experiments are recorded in the accompanying statement; Te=127, O=16.

	Initial volume. C.m.3.	Final volume. C.m.3.	TeO_3 taken. Grm.	TeO_3 found. Grm.	Error. Grm.
(1)	50	20	0·0102	0·0098	0·0004—
(2)	50	20	0·0102	0·0099	0·0003—
(3)	50	20	0·0102	0·0098	0·0004—
(4)	50	20	0·0102	0·0098	0·0004—
(5)	100	40	0·1000	0·0994	0·0006—
(6)	80	40	0·1001	0·1001	0·0000
(7)	100	20	0·1002	0·1001	0·0001—
(8)	50	20	0·1000	0·1003	0·0003+
(9)	50	25	0·5011	0·5008	0·0003—
(10)	50	25	0·5002	0·5006	0·0004+
(11)	50	25	0·5000	0·4998	0·0002—
(12)	50	20	0·5000	0·4994	0·0006—

The results of experiment agree fairly well with one another and with theory based upon the assumption that the atomic weight of the tellurium which we employed was 127. It is evident that the reducing action of the hydrobromic acid developed in the distillation is regular and that that agent is well adapted to the reduction of telluric acid to tellurous acid. The formation of tellurium tetrabromide in the concentrated acid liquid makes it impossible to tell by the colour when all the bromine has been distilled, but the evidence of the experiments goes to show that the boiling of the liquid from a volume of 50 c.m.³ to 25 c.m.³ is sufficient, while concentration from 100 c.m.³ to 20 c.m.³ apparently does no harm.

INVESTIGATIONS ON THE ALUMINIUM SULPHATE OF COMMERCE.

By H. VON KÉLER and G. LUNGE.

An aluminium sulphate used in turkey-red dyeing should not contain more than 0·001 per cent of iron. To produce a sulphate more free from iron would be useless, since the influence of iron up to the above limit is quite trifling. But if this limit is exceeded, a minimal further addition of iron has a decidedly injurious effect.

It does not here depend solely upon the total quantity of iron, but upon its stage of oxidation. Ferrous salts are less hurtful than ferric compounds. The presence of zinc, which is certainly rarely detected in commercial aluminium sulphates, has an injurious effect upon the colour. In the choice of a sulphate it is therefore best always to select the sample poorest in iron and free from zinc.

II. *Tissue-Printing.*—The experiments were made in the print-works of Cunz, Wettler, and Forrer, at Blumenegg, near Rorschach. Acetates were made from the samples of sulphate, and steam-alizarin reds and roses were printed with them. In spite of the different proportions of iron in the mordants used, the shades both of red and rose were equal. A proportion of iron up to 0·00524 per cent has therefore no injurious effect upon the purity of the colours. An aluminium sulphate offered for sale will scarcely contain a larger amount of iron.

A second series of experiments was made with aluminium sulphates, in which the proportion of iron had been artificially raised to 1 per cent. Even this abnormal quantity of iron produced no injurious effect upon the shades of printing.

This unexpected result may perhaps be explained by the consideration that in printing, as compared with turkey-red dyeing, only very slight quantities of mordant are applied to the fibre, whence the salts of iron are presen in a quantity too trifling to affect the shades.

We may lastly observe that some experiments were made with Persian berries, the yellow of which is regarded as of all printing colours the most sensitive to iron. Swatches printed with the smallest and highest proportions of iron (within permissible limits) showed no difference in the tone of the yellow. Hence a proportion of iron in the aluminium sulphate up to 0·005 per cent is unimportant in tissue-printing.—*Zeitsch. fur Angewandte Chemie.*

THE VOLUMETRIC DETERMINATION OF FORMIC ACID.

By A. LIEBEN.

The author employs for this determination the property of formic acid to reduce pemanganate. Saint Gilles formerly effected the determination of formic acid by oxidising it with permanganate in an alkaline solution, and then completing the titration in an acid solution. Lieben maintains that the oxidation of formic acid by permanganate in an acid liquid cannot be utilised for a quantitative determination either at ordinary temperatures or in heat. The values obtained are always too low.

On the other hand, it is practicable to obtain a complete oxidation of formic acid in presence of sodium carbonate so as to admit of a volumetric determination. It is indifferent whether the process is conducted at ordinary temperatures or in heat, and the quantity of the excess of sodium carbonate added is also unimportant. The oxidation takes place according to the following equation:—

$$3KCHO_2+2KMnO_4=2MnO_2+2K_2CO_3+KHCO_3+H_2O.$$

The final point of the titration is not easily recognised since the red colour produced towards the end of the reaction disappears but slowly. It is therefore necessary to wait for some time in order to be convinced of the permanence of the red colouration. The author when titrating in the cold allows the liquid to stand covered overnight in order to become satisfied of the completion of the process by the permanence of the red colour. If the titration is effected in the cold a much shorter time is sufficient.

The analyses quoted are satisfactory. The method is applicable for the determination of formic acid in a free condition or in its salts. It is of course useless in the

presence of other constituents which reduce permanganate.

The author has besides tested the method recommended by Scala. He finds that correct results can be obtained only if the excess of mercuric chloride added to the neutralised solution is very considerable. At least 50 times the weight of the formic acid will have to be present, or four times the quantity theoretically required.

It is also to be recommended not merely to heat in the water-bath for two hours, as Scala proposes, but six or eight hours. It is necessary *after filtration* to heat the filtrate for some time in the water-bath in order to be satisfied of the entire completion of the reaction. A slight turbidity may be disregarded, as 1 c.g. $HgCl_2$ corresponds only to about 1 m.g. formic acid.—*Zeitschrift fur Analytische Chemie.*

DETERMINATION OF BORIC ACID.

By R. HEFELMANN.

THE author has used several of the known methods, and communicated his experience.

The only direct determination of boric acid is founded upon the sparing solubility of calcium fluoboride. This method, however, does not yield absolutely sharp results, and cannot be utilised for the determination of boric acid in borax, since the sodium borate formed is likewise sparingly soluble in water. Hence the determination of boric acid in borax is generally effected in an indirect manner as loss, or it is calculated from the soda found. For this purpose we titrate a concentrated solution of borax with normal sulphuric acid, using tincture of litmus as indicator. Boric acid gives with tincture of litmus a vinous red colour, whilst a drop of sulphuric acid in excess produces an unmistakable onion-red colour.

C. Schwartz (*Pharm. Zeitung*, 32, 562) proposes Congo red as an indicator. If we add hydrochloric acid to the solution of a pyroborate coloured with a few drops of Congo red, the blue colouration does not appear until all the sodium pyroborate has been decomposed into sodium chloride, and free boric acid and free hydrochloric acid appear. Insoluble borates are dissolved by excess of hydrochloric acid, and the excess of the latter is titrated back with normal alkali, when the colour changes from blue to orange. Hefelmann prefers the use of litmus as compared with Congo red.

The method proposed by H. Will (*Zeitschrift*, xxviii., 100), according to which the free boric acid is titrated with baryta water, is, according to the author, suitable for technical purposes, but for more accurate determinations it is not satisfactory.

Among the indirect gravimetric methods the author obtained fairly concordant results by the hydrofluoric sulphuric acid method. 0·5 grm. of the borax, finely powdered and dehydrated by ignition (or of a mixture of borate and boric acid), is digested for three hours on the water-bath in a platinum crucible of the capacity of 50 c.c. with 10 c.c. of hydrofluoric acid. The hydrofluoric solution is evaporated down to one-half, and at intervals of half an hour a c.c. of pure concentrated sulphuric acid is poured into the covered crucible. As soon as vapours of hydrofluoric acid cease to escape, the sulphuric acid is driven off over a small flame and the crucible is finally heated to dull redness. Hereby all the boric acid is volatilised as boron fluoride, whilst the bases (only soda in case of borax) remain as sulphates. If in case of borax the soda is calculated from the sulphate, and its quantity is deducted from the original anhydrous borax, the difference shows the quantity of boric acid sought. This method may be also applied in presence of chlorides and sulphates if they have been determined previously to the boric acid.

The boric acid combined with soda as sodium pyroborate is determined by titration with normal sulphuric acid; the free boric acid then appears as the difference of the combined boric acid and the total boric acid as determined by the hydrofluoric method.

The method of H. Rose (Fresenius, "Quantitative Analysis," Sixth Edition, vol. i., p. 422) allows of the determination either of free or combined boric acid by fusion with sodium carbonate. Hefelmann made experiments in this direction both with borax and with sodium chloroborate, determining the carbonic acid escaping on fluxing the dehydrated salts with anhydrous sodium carbonate, and calculating from this the quantity of boric acid.

These experiments have not yielded satisfactory results. They showed that the success of the operation depends on the proportion of the quantities of borax and of sodium carbonate. According as both are present in equivalent proportions, or as the sodium carbonate is present in larger or smaller excess, the reaction ensues according to different equations. It must also be considered that on prolonged ignition sodium carbonate loses carbonic acid.

The determination of chlorine in such compounds as sodium chloroborate (apparently a pharmaceutical preparation) may without hesitation be effected by titration with a solution of silver. In very dilute hot solutions of boric acid and borax, silver solutions produce no precipitate, and in very dilute solutions the formation of silver chloride precedes that of silver pyroborate. The values obtained at a dilution of 1 : 1000 are some tenths of a per cent higher than those found by gravimetric analysis.

For the determination of small quantities of boric acid, Parmentier (*Comptes Rendus*, cxiii., 41) utilises the following reactions:—

1. Boric acid effects no change in helianthine which has been turned yellow by free alkali.

2. A solution of boric acid mixed with tincture of litmus gives on titration with soda-lye a characteristic change of colour, when all the boric acid has been converted into sodium biborate.

Not every kind of tincture of litmus can be employed in this titration. The ordinary tincture of commerce, even when purified by one of the known methods, shows no sharp final reaction. Orceine obtained by the oxidising orcine in presence of ammoniacal vapours gives better marked change of colour, but still leaves something to be desired. But the orceine prepared according to the proposal of De Luynes (*Ann. de Chimie et de Phys.*, 4, vi., 184) is found very suitable.

The application of the method pre-supposes that along with the boric acid liberated by a strong acid there should be present only salts of the alkalis and alkaline earths.

Parmentier made use of the method for determining boric acid in mineral waters, proceeding as follows:—

The mineral waters containing calcium hydrocarbonate and in part ferrous dicarbonate were evaporated down on the water-bath or over an open fire. The precipitates contained all the boric acid, and at the same time the chief quantity of the silicic, phosphoric, and arsenic acids. The deposits were dissolved in hydrochloric acid, and the solutions thus obtained were evaporated down at a low temperature, or in rarefied air over sulphuric acid and potash with any loss of boric acid.

The residue of the evaporation was rapidly heated to 100°, taken up with water and a little hydrochloric acid, and mixed with a slightly ammoniacal solution of ammonium nitrate. The precipitate formed contained the iron, alumina, manganese, the arsenic and phosphoric acids, whilst the boric acid remained in solution. The precipitate was filtered off, the filtrate distinctly acidified with dilute sulphuric or hydrochloric acid, and divided into two exactly equal parts. In one the acidity was determined volumetrically, using helianthine methyl orange as indicator; in the other half it was determined in presence of solution of litmus (prepared according to the method of De Luynes) with a standardised soda-lye free from carbonic acid. The quantity of boric acid present appears from the difference of the two titrations.

In order to demonstrate the accuracy of the method, the author prepared artificial mineral waters containing from 5 to 20 m.grms. boric acid. The quantities of boric acid employed were exactly recovered by means of this method.

A. K. Reischle (*Zeitsch. fur Anorgan. Chemie*) has also engaged in a verification of the various methods for the determination of boric acid.

Marignac's well-known method (Fresenius, "Quantitative Analysis," Sixth Edition, vol. i., p. 422) yielded decidedly unsatisfactory results. The above-mentioned method of H. Rose can yield approximately concordant results if certain precautions are observed.

G. Krüss and H. Moraht, who have employed various methods for determining boric acid when examining glucinum borates, have arrived at the same results concerning the methods of Marignac and Rose. They finally employed with success the method of Stromeyer, according to which the boric acid is separated as potassium fluoboride (*Liebig's Annalen*, 260, 180).

F. A. Gooch decomposes the borate with nitric acid or acetic acid in a special apparatus, and conveys the boric acid into a well-closed receiver by repeated distillation with methylic alcohol. The distillate is evaporated to dryness with a weighed quantity of recently ignited calcium oxide. The residue is ignited, weighed, and the boric acid sought for is calculated from the increase of weight.

Th. Rosenstadt recommends for the determination of the boric methyl ether ignited magnesia, which was also originally used by Gooch.

Whilst Gooch obtained by this procedure 100·16 to 101·37 per cent of the boric acid employed, the values obtained by Reischle varied from 90·8 to 101 per cent. On a qualitative examination of the residues from distillation, traces of boric acid were detected even after twelve repetitions of the distillation. A further source of error in the method depends on the difficulty of weighing exactly the ignited residue of calcium borate and excess of quicklime, as it readily absorbs carbonic acid and water.

The experiments of the author show, therefore, that the method of Gooch always gives fluctuating results, generally too low.

The above-mentioned method of Parmentier, according to the author, does not lead to useful results. The change of colour of methyl orange on titrating free sulphuric acid in presence of boric acid is too indistinct, especially if very dilute liquids are used for titration, as must be the case in determining small quantities of boric acid.

Similarly unfavourable results were obtained on determining boric acid as potassium borofluoride. Hereby a weighed quantity of borate was heated with hydrofluoric acid and potassium carbonate in a platinum retort with a platinum reflux condenser. The precipitate of potassium borofluoride obtained was washed either according to F. Stolba, with potassium tartrate, or according to H. Rose, with cold alcohol.

The author finally recommends the determination of boric acid by the loss of weight on volatilisation of the boron as ammonium borofluoride. Instead of treating the borate with hydrofluoric acid and sulphuric acid, Reischle proposes to mix it in a platinum crucible with six parts of re-sublimed ammonium fluoride, and to heat slowly when the chief quantity of the ammonium borofluoride is volatilised. When cold, sulphuric acid is added, and its excess is driven off by heat along with the last traces of boron fluoride or of ammonium borofluoride. After a single treatment in this manner a sulphate is obtained completely free from boracic acid. The author obtained very satisfactory results on the analysis of pure borax and of a mixture of weighed quantities of boric acid and lime.

The use of this method is always advisable if the base can be weighed as sulphate. If this procedure is not applicable, the author recommends the determination of the proportion of base in another manner, and that of water of crystallisation as accurately as possible by a considerable number of experiments, and to calculate the boric acid as difference.—*Zeitschrift für Analytische Chemie.*

A METHOD FOR DETERMINING CALCIUM OXIDE IN QUICKLIME.*

By W. E. STONE and F. C. SCHEUCH.

The value of quicklime is based upon the amount of calcium oxide which it contains. This value may be diminished by the presence of other substances originally present in the limestone, consisting usually of magnesia, alumina, silica, and iron; by incomplete ignition in the lime-kiln, on account of which some calcium carbonate fails to be converted into calcium oxide; and lastly, by a partial "slaking," by which a portion of the calcium oxide reverts to calcium carbonate.

An analysis of quicklime, therefore, should show not only the amount of calcium present in distinction from other elements, but should distinguish between the calcium as oxide and other forms of combination. The customary gravimetric method, based upon solution of the calcium compounds in acids, precipitation as calcium oxalate, ignition, &c., attains only the first of these requirements and affords no data for judging of the original condition of the calcium thus found. Consequently this method may furnish erroneous conclusions with regard to the commercial value of the material examined.

The method here proposed enables one to determine with a high degree of accuracy and rapidity the actual amount of calcium oxide in quicklime. It is based upon the well-known fact that the alkaline earths form definite compounds with sucrose, called saccharates. Several such compounds are known with barium and strontium. With calcium oxide sucrose forms at least three compounds, the mono-, di-, and tri-calcium saccharates, containing respectively one, two, and three molecules of calcium oxide to one of sucrose. The two first are formed when quicklime is dissolved in the cold in a sucrose solution. On heating this to boiling, a precipitate is thrown down consisting in the main of the tri-calcium saccharate.

Numerous authorities may be quoted with regard to the solubility of calcium oxide in sucrose solutions, of which the two following will suffice for citation:—

Berthelot (*Ann. Chim. Phys.*, [3], xlvi., 176) gives the maximum solubility in solutions of sucrose of varying strength.

Grms. sugar in 100 c.c.	0·096	0·400	1·058	1·386	2·000	4·850
CaO dissolved ..	0·154	0·194	0·281	0·326	0·433	1·031

The following data are from Schatten (Von Lippmann, "Die Zucker-Arten," 109):—

In 10 Grms. of Sugar Solution of different Percentages.

Per cent	1	4	8	12	16
Grms. CaO dissolved	0·029	0·080	0·160	0·271	0·394

Numerous other references indicate the ready solubility of calcium oxide in sucrose solutions, and the apparent possibility of applying this fact to the separation of the actual calcium oxide from the other constituents of quicklime led us to make the following studies:—

1. The conditions under which calcium oxide is dissolved in sucrose solutions:—

Lamy (*La Sucrerie Indigene et Coloniale*, xi., 19) has shown that solubility varies inversely with the temperature. Ten litres of 10 per cent sucrose solution, at the

* Contributions from the Chemical Laboratory of Purdue University. From the *Journal of the American Chemical Society*, xvi., No. 11.

given temperatures, dissolved the stated amounts of calcium oxide.

Temperature °C.	0°	15°	30°	50°	70°	100°
Grms. CaO dissolved ..	250	215	120	53	23	15·5

For our experiments, pure calcium oxide was prepared by igniting pure calcium carbonate to a constant weight. It was found by repeated experiment that 1 grm. of this material was easily soluble in 150 c.c. of a 10 per cent sucrose solution after agitating fifteen to twenty minutes at ordinary temperature. To accomplish perfect solution it was necessary that the material be finely pulverised. If heat were employed, the lime was converted into a pasty insoluble mass, which, however, dissolved on cooling.

2. The degree of solubility of calcium oxide in sucrose solution. Repeated experiments gave the following results:—

One grm. of pure CaO was only partly dissolved in 100 c.c. of a 5 per cent sugar solution.

One grm. of pure CaO was only partly dissolved in 150 c.c. of a 5 per cent sugar solution.

One grm. of pure CaO was only partly dissolved in 100 c.c. of a 10 per cent sugar solution.

One grm. of pure CaO was completely dissolved in 150 c.c. of a 10 per cent sugar solution.

From these results it appears that not less than 150 c.c. of a 10 per cent solution of sucrose could be safely employed to dissolve the calcium oxide in 1 grm. of quicklime.

3. Behaviour of other constituents of quicklime toward sucrose solutions:—

Besides calcium oxide, quicklime usually contains more or less iron, alumina, magnesia, and silica. In addition to these, calcium carbonate may also be present. The behaviour of these toward sucrose solutions was studied in detail, with the following results:—

Magnesia.—Pure magnesium oxide, specially prepared, was treated with a 10 per cent solution of sucrose. 150 c.c. of the latter, after shaking with 1 grm. of magnesium oxide for thirty minutes, were filtered and treated with ammonia and sodium phosphate, but only the faintest turbidity resulted. Again, 1 grm. of magnesium oxide was shaken with 150 c.c. of sucrose solution, filtered, and the filtrate titrated with standardised hydrochloric acid, and an equivalent of 0·001 grm. of magnesia was found, or one-tenth of one per cent. These results show that magnesia is not appreciably soluble under the given conditions. Indeed, the existence of a compound between magnesia and sucrose is doubted. On the other hand, magnesia is said to be freely soluble in a solution of calcium oxide in sucrose (Von Lippmann, "Die Zucker-Arten," 148). To test this point, mixtures of pure magnesium and calcium oxides were treated with sugar solutions as follows:—One half grm. of each were mixed and shaken with 150 c.c. of sugar solution. A considerable portion of the material was insoluble. We filtered, and titrated the filtrate with standardised acid, the result being an exact equivalent of the calcium oxide employed. Again, one-half grm. of each were mixed and treated with sugar solution as before. We filtered, and precipitated the calcium from the filtrate by means of ammonium oxalate. The filtrate from this showed only slight turbidity when treated with ammonium and sodium phosphate. These results show that magnesium oxide is not soluble to an appreciable degree in sucrose solution containing calcium oxide, under the stated conditions.

Alumina was found quite insoluble, no appreciable amount being found in the filtered sucrose solution.

Calcium carbonate was also insoluble to any appreciable degree in the 10 per cent sucrose solution under the stated conditions.

Ferric oxide shaken with 10 per cent sugar solution was also insoluble. Schachtrup and Spunt (*Pharm. Cent. Halle*, xxxiv., 148) mention that ferric oxide inverts sucrose, but not in an alkaline solution. We have verified this by heating a small quantity of ferric oxide with a sugar solution; the latter soon acquired the power of reducing Fehling's solution. But when the same experiment was repeated with the addition of some calcium oxide, no inversion occurred. It is evident, therefore, that the iron contained in quicklime would not be affected by sucrose solution.

4. The determination of calcium oxide when dissolved in sucrose solution:—

Calcium oxide when dissolved under the preceding conditions admits of determination, either gravimetrically by precipitation as calcium oxalate, or volumetrically by titration with hydrochloric acid. Several comparisons of the two methods were made, using known amounts of pure calcium oxide, and while each were accurate to the extent of yielding the theoretical numbers, the volumetric method was found preferable on account of its greater rapidity. For the latter method, standardised hydrochloric acid of about fifth-normal strength was employed, using tropæolin or rosolic acid as an indicator.

5. Application of the preceding data to the analysis of quicklime.

Following the conclusions derived from the preceding tests, several samples of quicklime were analysed for calcium oxide. They were all in a fresh state and contained little calcium carbonate.

In each case approximately 1 grm. of the finely pulverised material was shaken with 150 c.c. of a 10 per cent sucrose solution during twenty minutes, the solution filtered, and the clear filtrate titrated with standardised hydrochloric acid. At the same time other portions of the same samples were dissolved in hydrochloric acid and the calcium determined in the usual way by precipitation as calcium oxalate. Following are the results:—

Sample.	Weight of quicklime taken. Grms.	Volume of 10 per cent solution of sucrose taken. C.c.	Per cent CaO by titration method.	Per cent CaO by gravimetric method.	Variation of volumetric method.
No. 1.. ..	1·020	150	92·12	93·00	−0·88
,, 2.. ..	1·090	150	91·90	92·28	−0·38
,, 3.. ..	1·006	150	92·15	93·10	−0·95
,, 4.. ..	1·108	150	95·01	95·90	−0·89
,, 5.. ..	1·023	150	87·30	87·70	−0·40
,, 6.. ..	1·232	150	91·70	92·30	−0·60

The results by the sucrose method were in each case slightly lower than by the gravimetric method, discrepancy which may be ascribed to a small amount of calcium carbonate present in the sample.

In quicklime which had become partially slaked this discrepancy would be still greater, since the sucrose method would indicate only the actual calcium oxide. Aside from this, the greater ease and rapidity of the latter recommends it in cases where the total calcium is present in the form of the oxide. An entire determination may thus be made in a half-hour with a degree of accuracy quite sufficient for all ordinary purposes.

THE CHOCOLATE NICKEL ORES OF NEW CALEDONIA.

By THOMAS MOORE, Nouméa.

UNTIL quite recently the principal New Caledonian nickel ores of any commercial importance were the now well-known green silicate, and to quite an insignificant extent the so-called chocolate nickel. This position of affairs has now every appearance of being greatly modified or perhaps reversed, and the future supply of ore will, without doubt, consist of a mixture of the two minerals, the chocolate predominating.

The occurrence of this chocolate ore has been known for a long time, but owing to its deceptive appearance and total dissimilarity to all other nickeliferous material, it has been for years discarded and thrown on the rubbish heaps as a worthless ferruginous substance. By degrees, however, its real value became known, and its extraction seriously undertaken, in some cases with disastrous results, as the ordinary deposits of oxide of iron and this mineral not only bear a great resemblance, but lie side by side, or even intruded in each other, so that it is impossible to judge by the eye where the one begins or the other ends, and it is only by a chemical examination that one can discriminate whether the material is nickeliferous or not. Up to this period, the designation "chocolate" very aptly described its appearance, and although the term is still used to include all the varieties, it can only be correctly applied to a certain number of them, the remainder being of various colours, *i.e.*, red, orange, yellow, and brown. It will be observed from the subjoined analyses that these minerals are of great importance from a metallurgical point of view, inasmuch as the comparatively small amount of magnesia favours the production of a fluid, easily fusible, and consequently clean slag, a state of things very difficult to realise with the green ores, containing, as they do, a large percentage of magnesia with but very little oxide of iron, and thus necessitating a large addition of flux and extra expenditure of fuel. The chocolate ores are for the most part of no definite composition, the ratio of the oxygen in the basis to that in the silica ranging from 1 :. 1·3 to 1 :. 0·6. When examined under the microscope they are seen to consist of a heterogeneous mass of various minerals, such as quartz, chromite, oxide of iron, steatite, and the green silicate, and when cautiously acted upon by dilute acids the intermixed oxide of iron is dissolved, leaving a green residue and giving a yellow solution containing only a little nickel. Their hardness is such that they may nearly all be marked by the thumb-nail, and some even admit of being crushed to a powder between the fingers. Very curious is the occurrence of pieces of brilliant green Garnierite in the body of these minerals, especially in the harder varities, as when examined the green has invariably been found to belong to the richest class of its kind, carrying from 30 to 40 per cent. of oxide of nickel. Exposure to atmospheric influences rapidly disintegrates them, the softer species crumbling to a powder, whilst the harder become cracked and fissured in all directions. Before the blowpipe they give off water and the colour darkens, but are either infusible or fusible at the thin edges with difficulty.

	1.	2.	3.	4.	5.	6.
SiO_2 ..	33·70	37·05	24·25	34·55	48·25	26·18
Chromite	1·20	1·21	0·25	0·20	0·62	4·11
Fe_2O_3 ..	19·09	16·92	42·50	10·10	18·40	25·17
Al_2O_3 ..	1·40	0·63		0·21	0·10	
NiO* ..	31·28	17·36	24·58	41·31	24·67	27 61
MgO ..	3·22	16·03		2·23		6·47
CaO.. ..	0·63	0·48	0·12	0·22	0·48	0·18
MnO ..	0·20		0·17	0·23		0·23
H_2O.. ..	9·21	10·51	8·48	8·64	7·33	8·64
	99·93	100·19	100·35	99·49	99·85	99·59

* Including a little CoO.

The above analyses commence with the deep chocolate-brown (1), and pass through the various shades, concluding with ochre-yellow mineral (6).

Determination of the Alkyl Anilines.—The method proposed by Reverdin and De la Harpe has been critically examined by W. Vaubel (*Chemiker Zeitung*), who finds it not absolutely satisfactory, but suggests as an improvement to dilute the acetic anhydride with xylol.

ON THE QUANTITATIVE DETERMINATION OF THE ORDINARY IMPURITIES OF THE "PURE NICKEL" OF COMMERCE.

By Dr. T. FLEITMAN.

THE ordinary contaminations found in nickel capable of being rolled—if prepared according to the author's process with an addition of magnesium—are iron, copper, cobalt, and traces of zinc, constituents derived from crude nickel (cubic nickel), from which sheet nickel has been obtained. If it has been produced by any of the other procedures which have subsequently been devised in imitation of mine, the sheet nickel often contains considerable quantities of manganese in addition to the above-named metals.

The determination of the constituents can be most rapidly and easily effected as follows:—

Dissolve a quantity of the sample (in general not less than 5 grms.) in nitrohydrochloric acid, and destroy the excess of nitric acid by repeated evaporation with hydrochloric acid.

On filtering the solution it appears whether silica or carbon was present; if so, they can be determined if requisite.

By the careful and gradual addition of dilute sodium carbonate to the filtrate and subsequent ebullition, an experienced chemist can easily separate the small quantity of iron present (in general not above 1 per cent) without the simultaneous precipitation of cupric oxide or nickelous oxide in a ponderable quantity. The complete separation succeeds more easily, if close upon the entire separation of the ferric oxide a drop of acetic acid is added before boiling.

The ferric precipitate is filtered off, dissolved from the filter in hydrochloric acid, and the ferric oxide is precipitated with ammonia. If any copper appears to have been thrown down it can be readily added to the main quantity of copper to be obtained subsequently after it has been thrown down *alone* by acidulating the ammoniacal solution.

After eliminating the iron from the main solution, to which a drop of hydrochloric acid has been added, the copper is precipitated by adding drop by drop a saturated solution of sulphuretted hydrogen. The complete precipitation is easily recognised, but any drop of the sulphuretted hydrogen water in excess must be avoided, lest zinc or nickel should be simultaneously thrown down from the faintly acid—almost neutral—solution.

After separating the copper, which is determined in the customary manner, we precipitate the zinc as zinc sulphide by introducing more sulphuretted hydrogen in the cold. After filtration the precipitate is at once dissolved away from the filter with hot hydrochloric acid, and then precipitated as zinc carbonate.

After the filtrate from the zinc sulphide has been boiled to expel sulphuretted hydrogen, we proceed, for the more precise determination of the manganese and cobalt present in the solution, according to a method which I previously recommended in this journal for the determination of small quantities of cobalt in nickel (*Zeit. Anal. Chemie*, xiv., 76). It consists in separating the two above-named metals together as higher oxides, along with a small part of the nickel from the main mass of the nickel by gradually adding, to the neutral solution of nickel at 60°—80°, weakly alkaline sodium hypochlorite. There then falls firstly all the manganese as brown manganic oxide, next the cobalt as blackish-brown peroxide, and lastly, the nickel as deep black peroxide. The commencement of the precipitation of this last is marked by a striking liberation of oxygen as well as by the change of colour.

After boiling and filtering the precipitate of the mixed oxides thus obtained they are dissolved on the filter in hot hydrochloric acid, the excess of chlorine is expelled,

the solution is rendered acetic, and the cobalt and nickel are precipitated in heat as sulphides by the introduction of sulphuretted hydrogen. The sulphides are dissolved in nitric acid in the usual manner for the determination of cobalt, and precipitated with potassium nitrite. On working carefully, the mixture of the two metals thus obtained consists of nearly equal quantities of cobalt and nickel, in which the cobalt can be very accurately determined by potassium nitrite, whilst it is almost impossible if 50 to 100 parts of nickel are present to 1 part of cobalt.

In the filtrate from the nickel and cobalt sulphides all the manganese is present as manganous oxide, which may be directly precipitated with sodium carbonate, and determined as usual. Any use of an ammonium salt must be avoided, as ammonia interferes with the precipitation of the peroxides. Neutralisation, if necessary, must be effected with sodium or potassium carbonate. Traces of arsenic, antimony, and tin accompany the iron. Lead is obtained along with the copper. Zinc, if not in large quantity, does not interfere with the determination of cobalt and manganese.—*Zeit. Anal. Chemie*, xxxiii., 335.

HIGHER RESEARCH IN CHEMISTRY.

City and Guilds of London Institute for the Advancement of Technical Education.

The following scheme for the administration of the grant of £150 a year has been provided by the Salters' Company for the encouragement of Research in Applied Chemistry in connection with the City and Guilds of London Institute. (The first award will be made early next year):—

The Grant shall be applied to founding one or more Fellowships entitled "Salters' Company's Research Fellowships" for the encouragement of Higher Research in Chemistry in its relation to Manufactures.

The Research Fellowships shall be awarded by the Executive Committee of the Institute, with the consent and during the pleasure of the Court of the Salters' Company, in accordance with the present scheme, or with such modifications as the Court of the Company may from time to time approve.

The amount of the grant attached to each Research Fellowship shall be determined by the Executive Committee, with the approval of the Court of the Salters' Company, with reference to the nature of the Research, the time required to complete it, and the merits of the candidate.

The Executive Committee shall appoint a Special Committee to report on the selection of candidates and the progress of Researches, and such Committee shall include the representative or representatives for the time being of the Salters' Company on the Executive Committee.

The Executive Committee shall each year apply the sum provided by the Salters' Company to the award of Fellowships to British born subjects, of a value not exceeding £150, (*a*) to students of the Institute who have completed a full three years' course of instruction in the Chemical Department of the Central Technical College, or (*b*) to candidates duly qualified in the methods of Chemical Research in its relation to Manufactures without restriction as to age or place of previous study.

The Executive Committee shall report to the Salters' Company the award of each Research Fellowship, and at the close of each session shall report the results or progress of the Research or Researches undertaken during the session.

A Research Fellowship may be renewed for a second and third year, but shall not be held by anyone for more than three years.

The holders of Research Fellowships shall devote their whole time to the prosecution of Research, unless otherwise sanctioned by the Executive Committee; and shall report as required on their work.

The Researches shall be carried out at the Institute's Central Technical College, and the holders of Research Fellowships shall be subject to the regulations of the College and the supervision of the Board of Studies.

Applications for Salters' Company's Research Fellowships shall be made in writing addressed to the Honorary Secretary of the Institute, at the Head Office, and shall state the nature of the Research proposed to be undertaken, and the qualifications of the candidate.

F. A. Abel, Chairman of the Executive Committee.
John Watney, Honorary Secretary.

PROCEEDINGS OF SOCIETIES.

ROYAL INSTITUTION OF GREAT BRITAIN.

General Monthly Meeting, Monday, December 3, 1894.

Sir James Crichton Browne, M.D., LL.D., F.R.S., Treasurer and Vice-President, in the Chair.

The following were elected Members of the Royal Institution:—The Rev. J. O. Bevan, Messrs. H. T. Brown, F.R.S., H. S. Keating, G. Lindo, S. Morse, E. Steinkopff, G. J. Stoney, F.R.S., C. L. Tuckey, M.D., A. E. Western, C. Wightmann, and G. W. Wolff, M.P.

The Special Thanks of the Members were returned to Mr. Ludwig Mond and Dr. William S. Playfair for Donations towards the fund for the Promotion of Experimental Research at Low Temperatures.

The following Lecture Arrangements were announced:—Professor J. A. Fleming, F.R.S., Six Lectures (adapted to a Juvenile Auditory) on the "Work of an Electric Current;" Professor Charles Stewart, Twelve Lectures on "The Internal Framework of Plants and Animals;" Mr. William Samuel Lilly, Four Lectures on "The English Humourists of the Nineteenth Century;" Mr. L. Fletcher, F.R.S., Three Lectures on "Meteorites;" Dr. S. R. Gardiner, Three Lectures on "Three Periods of Seventeenth Century History." 1. The Monarchy. 2. The Commonwealth. 3. The Restoration; Dr. E. B. Tylor, F.R.S., Two Lectures on "Animism;" Mr. Lewis F. Day, Three Lectures on "Stained Glass Windows, and Painted Glass from the point of view of Art and Craftmanship;" Dr. A. C. Mackenzie, Three Lectures on "Hänsel and Gretel," an opera by E. Humperdinck (with musical illustrations); The Right Hon. Lord Rayleigh, Six Lectures.

The Friday Evening Meetings will commence on January 18, when Professor Dewar will deliver a discourse on "Phosphorescence and Photographic Action at the Temperature of Boiling Liquid Air." Succeeding discourses will probably be given by Sir Colin Scott Moncrieff, Mr. Henry Irving, Dr. G. Sims Woodhead, Mr. Clinton T. Dent, Professor A. Schuster, Professor A. W. Rücker, Professor Roberts-Austen, Professor H. E. Armstrong, The Right Hon. Lord Rayleigh, and other gentlemen.

Chemical Detection of Horse-Flesh.—W. Brautigarn and Edelmann (*Pharm. Central-Halle*) utilises the reaction of the glykogen always present in horse-flesh with iodine. They comminute 50 grms. of the flesh under examination as finely as possible, and boil it for an hour with four times its weight of water. A portion of the filtered liquid when cold is carefully mixed with dilute nitric acid (1 : 1) in order to separate most of the albumenoids and to destroy colouring matters. It is then superstratified with solution of iodine, prepared in heat and as saturated as possible. If horse-flesh is present there appears at the surface of contact of the two liquids a ring of a burgundy-red or violet. This reaction is not produced with the flesh of the ox, swine, calf, sheep, dog, or cat.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxix., No. 21, November 19, 1894.

The Session of the Academy was broken off on account of the funeral of the Czar.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. xi.-xii., Nos. 18 and 19.

On Triacetyl Gallic Acid.—(Reply to Hugo Schiff).—A controversial paper of little scientific importance.

On Triacetyl Gallic Acid.—P. Sisley.—A paper in evident connection with the foregoing. The author threatens to resume the subject in an early communication.

Quantitative Composition of the Creosotes of Oak and Beech Wood.—A. Béhal and E. Choay.—The substance of this paper has been already noticed.

On Piceine, a Glucoside of the Leaves of Pinus picea.—M. Tanret.—Already noticed.

On a New Glucosane, Lævo-glucosane.—M. Tanret.—This compound is obtained by the action of baryta upon piceine. This compound does not reduce Fehling's liquor and does not ferment with beer-yeast. If heated with dilute acids it is transformed into ordinary glucose, dextro-rotatory, a reducer and capable of fermentation.

Determination of Boron.—Henri Moissan.—This valuable paper cannot be reproduced without the accompanying figure.

Toxicological Detection and Determination of Arsenic.—M. Barillot.—Already inserted.

Determination of Total Nitrogen in Urine.—H. Moreigne.

Determination of Total Sulphur in Urine.—H. Moreigne.

Revue Universelle des Mines et de la Metallurgie.
Vol. xxviii., No. 2.

A New Gas in the Atmosphere, probably Elementary.—From the CHEMICAL NEWS.

Analysis of Pure Nickel or the Laminated Nickel of Commerce.—Dr. Th. Fleitmann (*Zeit. Anal. Chemie*).

Sodium Thiosulphite as a Type Material for Iodometry.—Prof. C. Meinecke (*Chem. Zeitung*).—The author, in endeavouring to obtain absolutely pure thiosulphite, found the following process most satisfactory. The crude salt is ground up in absolute alcohol, or in a mixture of alcohol and ether, which is then removed by the filter-pump. The mass is lastly washed with ether and dried in the open air. The product contained from 99·80 to 99·99 of the pure salt.

Determination of Phosphorus in a Thomas-Gilchrist Slag in different Industrial Laboratories.—P. Tabary.—The results varied from 2·10 to 1·71 per cent.

The Process of Digestion of Food in Animals and Plants.—A Free Lecture on this subject, with lantern illustrations and experiments, will be given by Prof. W. D. Halliburton, M.D., F.R.S., at the Theatre of King's College, London, on Wednesday next, December 12th, at 7 p.m.

MEETINGS FOR THE WEEK.

MONDAY, 10th.—Society of Arts, 8. (Cantor Lectures). "Modern Developments in Explosives," by Prof. Vivian B. Lewes.
—— Medical, 8.30.

TUESDAY, 11th.—Institute of Civil Engineers, 8.
—— Medical and Chirurgical, 8.30.
—— Photographic, 8.

WEDNESDAY, 12th.—Society of Arts, 8. "Manufacture of Salt," by Thomas Ward.
—— Pharmaceutical, 8.30.

THURSDAY, 13th.—Royal, 4.30.
—— Mathematical, 8.
—— Institute of Electrical Engineers, 8. Anniversary.

FRIDAY, 14th.—Physical 5. "Students' Apparatus for Determining the Mechanical Equivalent of Heat," by W. E. Ayrton and H. C. Haycraft. "Glow Lamp Tests and the Measuring Instruments," by W. E. Ayrton and E. A. Medley.
—— Astronomical, 8.

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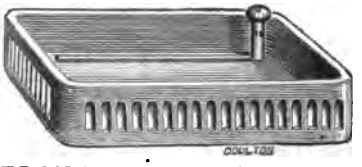

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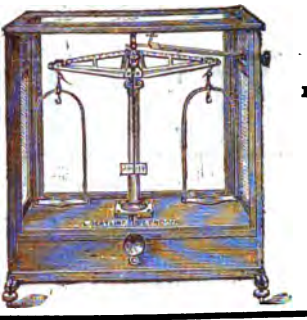

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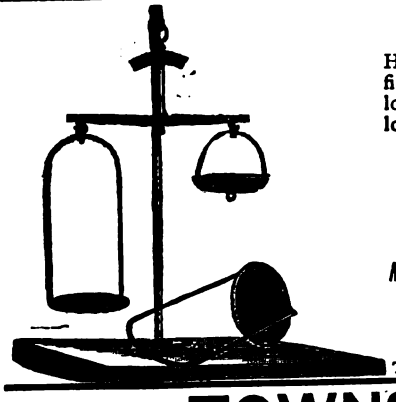

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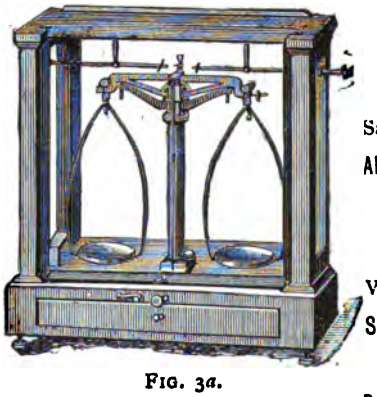

FIG. 3a.

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THE CHEMICAL NEWS.

VOL. LXX., No. 1829.

ON THE ORIGIN OF NITRIC ACID.

By Dr. T. L. PHIPSON,

Graduate of the Faculties of Science and Medicine of the University of Brussels; Fellow of the Chemical Societies of London, Paris, Antwerp, &c.

ONE of the most striking facts in the whole range of chemistry is that the two substances, ammonia and nitric acid, so essentially opposite in character, are readily convertible one into the other.

For instance, in one of my recent experiments, liquid ammonia, somewhat diluted, was simply poured into a solution of permanganate of potash and the mixture allowed to remain for some days. The liquid being then filtered from the hydrated peroxide of manganese, and allowed to evaporate spontaneously in a warm room, produced crystals of *nitrite* and *nitrate* of potash. If the ammonia is in excess, the nitrite predominates; if the permanganate is in excess, the nitrate alone is obtained.

Again, if zinc or tin be dissolved in dilute nitric acid, the liquid produced yields *ammonia*, a fact that has long been known.

In my note "On the Nature of Nitrogen" (CHEMICAL NEWS, vol. lxix., p. 207), I stated incidentally that in nature *nitrates* are "undoubtedly the *residues of organic life*." I will now look a little closer into this question.

A certain quantity of nitrogen is supposed to be extracted year by year from the atmosphere by the natural process known as "nitrification." In what does this process consist? It has occupied the thoughts of many eminent chemists in all parts of the world, especially since the days of Napoleon Buonaparte. Many are the theories that have been put forth to explain it—porous bodies, catalysis, electricity, bacteria, &c.,—and we may safely assert that hitherto it has remained unexplained. No one seems to have realised that this process is universal, that it occurs constantly everywhere. But it is only in certain countries where rain is scarce that the resultant nitrates are easily discovered; for instance, certain parts of India, Peru, Egypt, Arabia, China, Persia, Kentucky, Les Landes (France), &c. Where the climate is dry, the nitrates are seen to effloresce on the soil; in all other parts they are washed away by the meteoric waters as rapidly as they are produced, and find their way into the rivers.

In my opinion nitrification simply consists in the oxidation of ammonia; for in a series of experiments I made many years ago with the view of forming saltpetre artificially by passing air through various bodies, I never obtained any nitrates unless some ammonia-yielding substance was present, though, doubtless, traces might be obtained from the ammonia always present in minute quantity in the air.

Now, ammonia is not only a volcanic product, but an *organic residue*—a secretion that has found its way into the artificial strata of the earth ever since life appeared upon the globe.

All nitrates are due to ammonia, and ammonia is a residue of animal and vegetable life, *but it is also a volcanic product*, like carbonic acid.

Ammonia kills plants, but nitrates are absorbed by all, and we find them in considerable quantity in the nettle, the tobacco, the sunflower, &c. In an analysis I made of a sample of Virginia tobacco-leaf (grown upon a soil without manure), which arrived at my laboratory just as it was taken from the soil, the substance, when heated in a platinum crucible, deflagrated in a very notable manner during incineration.

Nitrates are absorbed as such from the soil, and in the plant cell they are reduced, deprived of their oxygen, which is secreted into the atmosphere by the plant, and their nitrogen enters into the composition of albuminous bodies, which, on the final decay of the plant, are reduced to ammonia.

Liebig, in his well-known "Principles of Agricultural Chemistry" (p. 20), says:—"There is every reason to believe that in the process of vegetation nitric acid can replace ammonia as a source of nitrogen." But I must go much further than that, for I have convinced myself that *ammonia is converted into nitric acid before its nitrogen can be assimilated, and that ammonia will kill or injure the plant unless this conversion can take place.*

In seeking, therefore, to discover the origin of nitric acid in nature we are compelled to ask, *What is the origin of ammonia?*

Ammonia is found among the products of volcanic action, and the celebrated chemist Wöhler set up the hypothesis that its presence in the gaseous emanations of active volcanos is due to the action of steam upon deposits of *nitride of silicium*. In considering the boracic acid *lagunes* of Tuscany, it would have been easy, also, to have imagined it due to deposits of nitride of boron. But unfortunately for this notion deposits of such artificial products have never been met with in nature; and it is quite as possible that volcanic ammonia may be of organic origin, like that of the vast guano deposits of our own time, or like that derived from coal or petroleum, &c. Though traces of ammonia have been found in all mineral springs rising through secondary and tertiary strata, it has never been detected in the water of springs rising and flowing directly from the primitive rocks, such as granite. Nevertheless it has recently been found in the mineral apophyllite.

At the present time the average amount of ammonia in our atmosphere is to that of the carbonic acid as 3 is to 100; and this amount was considered by Liebig to be sufficient to supply the whole of the nitrogen required for plant life (and consequently for animal life) all over the globe. But he does not appear to have been aware of the *constant and universal production of nitric acid*. He believed that all the nitrogenous principles of plants are derived directly from ammonia, and many still hold the same opinion, whereas they are evidently derived from nitric acid, which itself is derived from ammonia by the natural process of nitrification.

The substance of plants and animals produces ammonia by its natural decay, and this ammonia, by being oxidised, produces nitric acid. The latter is again absorbed by plants, transferred to animals as albumin, &c., and finally reduced to ammonia by the decay of both.

If, therefore, we follow the atom of nitrogen through organic nature, we find that nitric acid is not the first-formed, since it must be derived from ammonia.

I was thus led to look upon ammonia as originally a volcanic product, like carbonic acid, and as the prime source of all nitrogen compounds.

In the primeval ages of the globe there could have been no nitric acid, nor even ammonia; but when the earth had cooled sufficiently—long before life appeared—ammonia could have existed in the volcanic products as it does at the present day. Later still, nitric acid formed from this ammonia was produced and plant life became possible. When organised beings perish and decay, their nitrogen and carbon return to nature as they originally existed; that is, as ammonia and carbonic acid.

Hence we see that *atmospheric nitrogen takes no part in the process of nitrification*, unless it be that comparatively small quantity which appears to be invariably converted into nitric acid during combustion, and by lightning; but this, after all, may be due to atmospheric ammonia.

These brief arguments, based upon direct chemical experiments, will, perhaps, again prove that questions of the

simplest nature are beyond the powers of science the moment they touch on the theory of creation.

It has been said of the ancient Britains, that those on the coast came from Gaul, but those who lived in the interior arose from the soil. This is, indeed, the safest opinion; for if we say they all came from Gaul, it will be asked, Where did the Gauls come from, if not from some more eastern country? And so we may go round the globe, through India and the New World, till, unlike Columbus, we get back to Britain again.

The Casa Mia Laboratory, Putney, S.W.,
December 6, 1894.

THE ABEL-TEST AND THE STANDARD OF SAFETY FOR MINERAL OIL.

By D. R. STEUART F.I.C., F.C.S.

The Scottish Section of the Society of Chemical Industry in their resolutions on flash-point said, "The Government Abel test is perfectly satisfactory for determining the lowest temperature at which inflammable vapours are evolved." I think now that this was rather a rash statement. I had my own apparatus, and never really compared its indications with any other, and I agreed to this resolution by an exercise of faith, and I suspect others did the same. I got another apparatus some time since, and I found that it gave invariably with different experimenters 5° below my first apparatus. Both are stamped by Board of Trade, one year between the dates. Another oil-work chemist tells me he has two apparatus with Board of Trade stamp, and that there is always 2° or 3° between the points got by them. I sent out the same sample of oil to six different chemists, and the results they got varied from 66° to 73°, and the time taken varied from one minute to nine minutes. This does not altogether depend on difference of apparatus, for I found two men of experience working according to the act, according to the best of their ability, with the same instrument and with this same sample of oil, gave the one 70° and the other 73°. These facts indicate that different instruments are not comparable, and also that the method is imperfect and does not give the same point even with skilled men who have comparable instruments. It may be that the Board of Trade are not doing their duty. The apparatus that gave with me the low result had a cup of copper instead of brass, but the capacities and thermometers were correct. I have not had time to compare thickness of metal with the schedule of the Act (1879) and go into the subject fully to see how reliable the apparatus would be if the schedule were strictly adhered to; but I hope other chemists will look into the matter and compare notes.

It is a great pity that the test is not what it should be; for the want of a reliable standard test-apparatus causes confusion in fixing the standard if the standard has to be altered. The matter is of such world-wide importance that it should be taken up by the Royal Society or the Chemical Society; and the test-apparatus should be fixed before fixing the standard. The standard must be fixed with a certain apparatus.

Perhaps I may make a few general remarks on flash-point taking. In taking the flash point of an oil we wish to get the lowest temperature at which, under any circumstances, it could evolve vapours to cause a slight explosion. The old Government open test therefore did not give the flash-point of the oil at all, for under certain circumstances the oil could give a serious explosion and take fire permanently 25° under the so-called flash-point by this apparatus. This of course is a matter of fact and not of opinion. But in a test we may tie ourselves down to the circumstances of a lamp. In a close tester the slower the heating the lower is the point got; and as it is the danger of an oil which is kept hours at the same temperature which we have to gauge, the slower the test the more truthful. But we cannot give more than ten minutes to the testing of an oil, and it should be recognised that the point got by such a test as Abel's in five or ten minutes is higher than the truth. Again, testing rapidly in this way, the larger the quantity of oil used the lower is the point got, and as the quantity in Abel test is much smaller than in a lamp, this also tends to make the point higher than it should be. Even Elliot's American apparatus uses a quantity much smaller than ordinary lamps. But it is inconvenient to have too large a cup, for sometimes only a small quantity of oil is available; so the quantity used in Abel apparatus might be adopted, but only recognising that the point got is too high, making the oil seem safer than it is. Again, in the Abel test the oil lies quiet, and a layer of heavy vapour gradually forms on its surface, slowly rising until it comes within reach of the flame. In common everyday life the danger is from a lamp with oil and air in reservoir shaken through each other by carrying the lamp. A method that mixes up air and oil together for an instant should be preferred, especially as we work too rapidly for the truth and with two small a quantity. The room for the vapours forming is too small in the Abel cup, particularly when it is high-flashing oil, for the oil expands very much on heating and reduces the air and vapour space. Putting down the light into the cup causes a rapid current of air over the surface of the oil, and will help to sweep away the vapours as they form and give too high a result. If the air and oil are not stirred together, there might be separate stirrers in the oil and in the air; but this would add to the expense. While the small quantity of oil used, the rapidity of testing, the oil remaining unstirred, the small air-space, and current caused by the test flame, all tend to make the point got by the Abel-test a little higher than it should be, there is one influence in the opposite direction. The little test lamp is connected by metal with the oil, and the heat from it may cause a flash, while the thermometer in the oil indicates a point below the true flash-point of the oil. This has greatest influence when the flash is high and the time taken long. After all, however, the Abel test is not far from the point we want, the point of incipient danger in an ordinary lamp. If it would only give a definite point with different men and different apparatus, it would be easy by experiment to fix its relationship to the points of danger in lamp, vessel, tank, &c. A large spill in a close cellar may take fire at below the Abel flash-point, or above the old open test according to the amount of draught through the place.

In fixing a standard it should be recognised that the only use of a standard at all is to save lives and property. This being the case, it would be better, as in Michigan, to make the standard one of rejection; that is, the oil to be rejected if it does not flash *above* a certain figure, the manufacturers being meant to keep their oil distinctly above the lowest minimum allowed. Also the lowest flash that can be got in a definite way is the truest, and therefore if the oil on several trials flashes once at the standard it is to be rejected—the lowest figure got being recognised as the true one and not the average of all.

The Abel-test professes to be an instrument of precision, and it is not. Oil which, tested in Scotland flashed at 105°, the standard, has been rejected by the Government officials, because in London it was found to flash at 104° to 104½°; and the Government instrument all the time is not definite within 5°. With another Government department oil that flashed in Scotland at 158° is rejected in London as flashing over 160°, and yet the Abel-test is not definite within 10° at these high temperatures.

The present Abel test is meant only to tell whether oil is of 72° or 73° flashing point. If 100 is fixed as standard, a method of testing, not to take more than ten minutes each test, must be defined to test oils of that flash, and this should be done before fixing the standard, otherwise 10° of safety might be lost at fixing the test.

The Abel apparatus is far too dear—5 guineas. An

apparatus should be adopted not costing more than 10s., and certainly not more than £1 at most, and which could be used by any shopkeeper with confidence and precision. The Elliot apparatus of America costs less than £1. If a scientific society were to take the matter up, it would be quite easy to discover such a test. Let a scientific society fix the test and the standard, so that an explosive mixture may never be found in the ordinary lamps of the people used with ordinary carelessness. Persons who use large expensive lamps, or the safety lamps of the London County Council, must buy Lighthouse oil of 150° flash, or risk their lives: our standard of safety cannot be made to suit them. But oil could be always labelled with the true flash-point for their convenience.

THE ACTION OF SUN'S RAYS ON BACTERIA AND FUNGI.

By W. R. BURNETT, F.C.S.

The special interest of the investigations on the action of the light on bacteria and fungi which have been made by Professor Ward, and which have appeared in the Chemical News (vol. lxx., p. 228) has led me to communicate what, from the peculiar favourable circumstances of the case, bears out to some extent the observations made by him on the action of light on bacteria and fungi. In connection with the River Thames he mentions that the number of bacteria per c.c. is decidedly and markedly less in the summer than in the winter, and he submits that, whether in view of the new facts elicited by him, it is not at least highly probable that the increased intensity of the light acting during a longer period through the summer days is a very powerful agent in keeping down the number of these bacterial and fungoid organisms in the water. When in Colombo, in the Island of Ceylon, I had, while acting for the City analyst, to make, along with the usual chemical tests, a biological examination of the town water each month, and was extremely surprised to find that in the *unfiltered* water the number of microbes on the nutritive gelatin rarely exceeded two colonies per c.c. of water after cultivation for 48 hours, results seldom if ever met with in English water supplies. The water did not appear to be a first class drinking water from a chemical point of view, containing on an average 0·005 grain per gallon of albumenoid ammonia and 0·04 grain per gallon of oxygen absorbed.

The great purity of the Colombo water as regards the presence of microbes is clearly explained by the investigations of Professor Ward, when it is pointed out that the water supply is obtained from extensive shallow surface water, which for the whole year is subjected to the rays of a tropical sun.

HAPLOPAPPUS BAYLAHUEN.

Messrs. Thomas Christy and Company, of London, have recently introduced a drug into commerce under the name of "Baylahuen," consisting of the leaves and stems of the *Haplopappus Baylahuen*, Remy, a plant belonging to the Aster family of the order Compositæ. It is indigenous to the Cordilleras of the Chilian province Coquimbo, and has been described by Remy (Gay's "Chilian Flora," iv., 42). The stem is woody and the leathery leaves are somewhat crowded together. They are from 2 to 2½ c.m. long, and at their broadest part, which is just above the middle, they are up to 1 c.m. broad. They are distinctly serrated, especially at the apex, and at their base they are somewhat sheathed.

The plant is especially characterised by a yellow, strong-smelling viscid substance, which not only covers the leaves but most parts of the stems. This substance causes the plant to appear as if it had been dipped into some resinous mass; but a section of the leaf shows that this covering forms a coherent crust, which, especially with young leaves, is greater in thickness than the layer of epidermal cells lying underneath.

Plants possessing this characteristic viscid covering were recently subjected to a special examination by Volkens (*D. Votan. Ges. Ber.*, 1890, viii., 120). According to this examination, it appears that this peculiarity is to be found among several of the Chilian Compositæ, especially those of the *Haplopappus* species. The viscous substance is generally secreted by hair-like glands. In the case of *Haplopappus Baylahuen*, these special glands consist of an agglomeration of numerous cells. The surface of the leaf is somewhat depressed round each gland, so that the glands as a rule do not protrude far above the surface of the surrounding epidermal cells. These gland hairs are closely distributed in large numbers over the upper and under side of the leaf.

The cells toward the outside of these gland hairs contain a small amount of crystals of oxalate of lime. It is to be remarked that all the membranes of the gland hairs, and also the cells at the base, do not consist of pure cellulose. They are insoluble in sulphuric acid. Iodine and sulphuric acid, or clor-zinc iodine, colours them intensely brown, and alkannin solution red, proving them to be of a suberous nature. The inner cells of the hair-like glands are lignified, which may be proved by the red colouration caused by phloroglucin and hydrochloric acid.

With regard to the anatomy of the drug in question, it may be further remarked that inside the leaf oil ducts were found filled with a resinous mass.

With reference to the microchemical properties of the secretion covering the drug, this is found to consist of a homogeneous layer with strong powers of refraction. In contact with water the secretion slowly forms a frothy mass, accelerated by warmth, as also by caustic potash. Absolute alcohol dissolves the secretion quickly and completely. A solution of alkannin in proof spirit colours it a beautiful red. The prussiate test recommended by Zimmerman (*Zeitsch. Wissenschafth. Markroskep.*, 1892, ix., 66), consisting of a mixture of equal volumes of concentrated prussiate solution in proof spirit and glycerin, colours it intensely blue. Thus one is justified in regarding the secretion as a combination of a resinous nature; at the present moment, however, reliable information cannot be given as to its exact composition, nor is it possible to obtain this until it is subjected to microchemical examinations.

In Chili the drug is used internally as a stimulant in cases of weak digestion, and as an emmenagogue. Outwardly it is used for healing wounds of animals. According to Baille (*Repertoire*, 1894, 165), the solution in 150 parts of water may be used as a splendid remedy for diarrhœa; it is also useful in cases of acute and chronic dysentery. Its medical properties are regarded as being due especially to the resinous combination contained in the drug. It is worthy of remark in this respect that in the genus *Grindelia*, which is closely related to *Haplopappus*, several species are covered with a viscid fluid, especially *Grindelia Robusta* and *Grindelia Glutinosa*, which are used in California for healing wounds.—*Chemiker Zeitung*, November 7, 1894.

Laboratory Accident.—According to the *Chemiker Zeitung*, Dr. Papendieck, chemist at the Lindenhof works, has been fearfully injured by the explosion of a compound destined for experimental purposes. His right hand was torn off, and he was also severely wounded in the left hand and the face.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 15th, 1894.

Dr. ARMSTRONG, President, in the Chair.

MR. A. E. TANNER was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. John Melrose Arnot, The Bally Paper Mills, Calcutta; Edward Elliott, Messrs. Reckitt and Sons, Hull; Harry Harris, The Pulo Brani Smelting Works, Singapore; Richard Ernest Kenyon, Ashville College, Harrogate; George Holman Kingdon, B.A., Taddyforde House, Exeter; Alexander MacFarlane, Patt Street, Ancoats, Manchester; Arthur Marshall, 65, Fairholme Road, West Kensington, W.

Of the following papers those marked * were read:—

*64. *Sulphonic Derivatives of Camphor.*" Part II. By F. STANLEY KIPPING, Ph.D., D.Sc., and WILLIAM J. POPE.

In this paper the authors describe the sulphonic bromides and chlorides of camphor, bromocamphor, and chlorocamphor which have been referred to in previous notes (*Proc. Chem. Soc.*, 1894, 163, 164). The behaviour of dextro-rotatory camphorsulphonic bromide has now been fully examined, and presents many features of interest.

Dextro-rotatory camphorsulphonic bromide,—

$$C_{10}H_{15}O\cdot SO_2Br,$$

is obtained in large orthorhombic octahedra, the crystallographic constants of which approximate very closely to those of dextro-rotatory camphorsulphonic chloride (*Trans.*, 1893, 548). The axial ratios of these sulphonic derivatives are as follows:—

$C_{10}H_{15}O\cdot SO_2Cl$ $a : b : c = 0{\cdot}9980 : 1 : 1{\cdot}0368$
$C_{10}H_{15}O\cdot SO_2Br$ $a : b : c = 0{\cdot}9816 : 1 : 1{\cdot}0249$;

the substances are therefore isomorphous, and consequently possess the same constitution. The sulphonic chloride almost invariably crystallises in tetrahedra, which, however, exhibit the positive and negative hemioctahedral forms; the hemihedral character of this substance is thus placed beyond doubt. The sulphonic bromide, on the other hand, usually crystallises in orthorhombic octahedra, which, from their geometrical form, would seem to be holohedral. The complete analogy between the bromide and chloride is demonstrated, however, by the fact that the bromide crystallises in tetrahedra on varying the conditions of crystallisation. A careful crystallographic comparison of the octahedral and tetrahedral forms of the sulphonic bromide showed conclusively that the difference between them is only one of habit, and is not due to a difference between their crystalline structures.

The inactive camphorsulphonic bromide which the authors have prepared has even less of the characteristics of a definite racemic modification than the corresponding sulphonic chloride. In the latter case the non racemic nature of the compound could not be demonstrated; in the case of the sulphonic bromide, the evidence against the existence of a true racemic modification is much more definite. By crystallising the inactive sulphonic bromide from ethylic acetate solution it may be partially resolved into the two oppositely active constituents. Further, the solution deposits large butterfly-shaped twin crystals; on examining these, the two wings are found to consist of the two oppositely active modifications. The lævo- and dextro-isomerides therefore twin together without forming a true racemic modification.

*65. "*Halogen Derivatives of Camphor.*" By F. STANLEY KIPPING, Ph.D., D.Sc., and WILLIAM J. POPE.

Seven new halogen derivatives of camphor have been obtained by heating the sulphonic chlorides and bromides which are described in the preceding and in other papers, at temperatures below 200°; the following is a list of the compounds thus prepared:—

Dextrorotatory chlorocamphor, $C_{10}H_{15}OCl$; inactive chlorocamphor, $C_{10}H_{15}OCl$. Dextrorotatory bromocamphor, $C_{10}H_{15}OBr$; inactive bromocamphor $C_{10}H_{15}OBr$. Dichlorocamphor, $C_{10}H_{14}OCl_2$. Dibromocamphor, $C_{10}H_{14}OBr_2$. Chlorobromocamphor,—

$$C_{10}H_{14}OClBr.$$

The bromochlorocamphor, which is doubtless produced on heating bromocamphorsulphonic chloride, has not yet been obtained in a state of purity, owing to the fact that secondary changes occur during its formation, giving rise to a somewhat complex product.

The dihalogen derivatives, and some of the monohalogen derivatives, notably the optically inactive bromocamphor, are very well characterised substances, and have been examined crystallographically; very interesting cases of dimorphism and of polymorphism have also been met with, and have been carefully studied.

*66. "*Dimethylpimelic Acid.*" By F. STANLEY KIPPING, Ph.D., D.Sc.

In preparing 2:6-diacetylheptane, for the purpose of studying its behaviour on reduction (*Trans.*, 1893, lxiii., 111), the author and Mackenzie obtained, as a by-product, an acid of the composition $C_9H_{16}O_4$, which, judging from its method of formation, was to be regarded as *aa'*-dimethylpimelic acid, $CO_2H\cdot CHMe[CH_2]_3\cdot CHMe\cdot CO_2H$. This acid, after careful purification, was obtained in well-defined crystals, melting at 80—81° (*Trans.*, 1891, lix., 569).

A short time after the publication of this paper, a dimethylpimelic acid, having, doubtless, the same constitution as the compound just mentioned, was prepared by Perkin and Prentice (*Trans.*, 1891, lix., 818), and also by Zelinsky (*Ber.*, xxiv., 3997); in both cases, however, the melting point differed from that given by the author and Mackenzie. Perkin and Prentice found the melting-point to be 74—76°, and, being cognisant of the earlier observations, they repeatedly re-crystallised their acid, but without effecting any change; Zelinsky, who appears to have overlooked the paper by the author and Mackenzie, gave the melting-point as 71—73°, and having obtained at the same time an oily acid of the composition $C_9H_{16}O_4$, he suggested that the latter was a stereoisomeric form of the crystalline acid.

These statements having thrown some doubt on the accuracy of the observations made by the author and Mackenzie, and the whole matter being in an unsatisfactory condition, the *aa'*-dimethylpimelic prepared by the hydrolysis of ethylic dimethyldiacetylpimelate was again examined.

The crude crystalline product began to soften at 52—58°, and usually liquefied completely at about 70°; when repeatedly re-crystallised the melting-point gradually rose, and finally an acid melting at 80—81° was obtained in a state of purity; this acid was identical with that (m. p. 80—81°) previously described.

The crystalline fractions of lower melting-point were found to have the same composition as the pure acid melting at 80—81°, a fact which indicated the presence of a stereoisomeric form, but all attempts to isolate such a compound by fractional crystallisation were unsuccessful. Portions melting from 55° to 70° were therefore treated with phosphorus pentachloride and aniline successively, and the products submitted to careful fractional crystallisation; in this way two anilides were isolated, one melting at 183—184°, the other at 154—155°, and on analysis both gave results agreeing with those required by the anilide, $NHPh\cdot CO\cdot CHMe\cdot[CH_2]_3\cdot CHMe\cdot CO\cdot NHPh$.

On hydrolysis they both gave an oily acid, which was ultimately obtained in well-defined crystals; the acid

from the anilide of higher melting-point was identical with the compound melting at 80—81°, whereas the product from the anilide melting at 154—155° was the sought-for stereoisomeride, and melted at 74·5—75°.

aa'-Dimethylpimelic acid, like the lower members of the series, exists therefore in two physically isomeric modifications, but the two forms are so similar in properties that their separation is not easily accomplished.

It seems probable that the acid described by Perkin and Prentice is identical with the modification melting at 74·5—75°, but the melting-point given by Zelinsky leaves the nature of his acid quite uncertain.

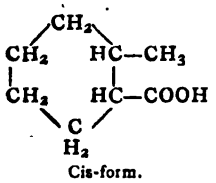
*67. "*Hexahydro-o-toluic Acid.*" By William Goodwin and W. H. Perkin, jun., F.R.S.

Some time since one of us, in conjunction with P. C. Freer (*Trans.*, 1888, liii., 208), prepared methylhexamethylene carboxylic acid (hexahydro-*o*-toluic acid) from the product of the action of methylpentamethylenedibromide on the sodium derivative of ethyl malonate, and described it as a colourless oil boiling at 235—236°. Recently Markownikoff has studied the reduction products of *o*-toluic acid, obtained by treating a boiling solution of the acid in amyl alcohol with a large excess of sodium, and has isolated a hexahydro-*o*-toluic acid, which boils at 240°, and solidifies on cooling, the melting-point of the pure acid being 41°.

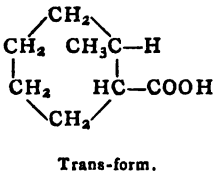
This wide difference in the properties of the synthetical acid and the acid obtained by reduction made it desirable to re-investigate the whole subject, with a view of determining the reason of the isomerism, and in order to do this we have prepared considerable quantities of both the acids, and carefully re-examined their properties, with the result that we find that the two acids are undoubtedly isomeric; the synthetical acid does not solidify at −10°, whereas Markownikoff's acid solidifies at ordinary temperatures with the greatest ease.

The anilides of the two acids also differ in a marked manner, as the anilide of the synthetical acid melts at 66°, that of Markownikoff's acid at 140°.

An examination of the formula of hexahydro-*o*-toluic acid at once reveals the fact that this acid can exist in two stereoisomeric forms,—



Cis-form.



Trans-form.

and it appears that the two acids mentioned above are in reality the two stereoisomeric forms of hexahydro-*a*-toluic acid.

This view is not improbable, since Baeyer and Rassow (*Annalen*, cclxxxii., 140) have shown that the somewhat analogously constituted *p*-phenylhexahydrobenzoic acid,

$$C_6H_5\cdot CH<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>CH\cdot COOH,$$

can be obtained in a cis and trans form.

In spite of a number of experiments, we have not succeeded in transforming the one modification into the other, probably because, owing to the low melting-point of the solid acid, it would be exceedingly difficult to isolate it from admixture with the liquid acid.

*68. "*The Addition of the Sodium Derivative of Ethylic Malonate to Ethylic Trimethylenedicarboxylate.*" By W. A. Bone, Ph.D., and W. H. Perkin, jun., F.R.S.

If a mixture of ethylic trimethylenedicarboxylate with the sodium derivative of ethylic malonate be digested in alcoholic solution a sodium compound is formed, which, when decomposed with acids, yields ethylic butane tetracarboxylate; additions having taken place thus, with disruption of the trimethylene ring,—

$$(COOC_2H_5)_2\cdot C<\begin{matrix}CH_2\\ |\\ CH_2\end{matrix} + CH_2(COOC_2H_5)_2=$$

$$=(COOC_2H_5)_2\cdot CH\cdot CH_2\cdot CH_2\cdot CH(COOC_2H_5)_2.$$

Similarly, when the sodium derivative of ethylic methylmalonate is employed in this reaction, ethylic methylbutanetetracarboxylate is formed (b. p. 240—250°, 55 m.m.).

This ethereal salt on hydrolysis yields the corresponding tetrabasic acid, which at 200° loses 2 mols. of carbon dioxide, and yields methyladipic acid,—

$$COOH\cdot CH(CH_2)\cdot CH_2\cdot CH_2\cdot CH_2\cdot COOH,$$

a colourless crystalline substance which melts at 64°, and is excessively soluble in water.

*69. "*The Reduction of Chlorides of Organic Acids.*" By W. H. Perkin, jun., F.R.S., and J. J. Sudborough, B.Sc.

The authors have found that aldehyds and alcohols may be readily prepared from acid chlorides by acting on these in moist ethereal solution with sodium, the yield obtained, especially in the case of the chlorides of the fatty acids, being satisfactory.

The following substances have been obtained by this method:—

n-Butyl aldehyd and *n*-butyl alcohol from *n*-butyryl chloride.
Isoamyl aldehyd and isoamyl alcohol from isovaleryl chloride.
Benzyl alcohol from benzoyl chloride.
o-Tolyl alcohol from *o*-toluic acid chloride.

This reaction is being carefully investigated in order to determine in what direction it is applicable, and with the object of finding the exact conditions for obtaining the best yields.

70. "*ββ-Ethyl Methyl Propionic Acid,*—

$$C_2H_5CH(CH_3)CH_2\cdot COOH."$$

By W. H. Bentley, B.Sc.

This acid, which is required for some experiments in connection with the fusion of camphoric acid with potash, has not been described. Its preparation and properties form the subject of the present paper.

Methyl ethyl ketone was reduced by sodium in moist ethereal solution, and thus converted into methyl ethyl carbinol. This, when treated with iodine and phosphorus, yielded secondary butyl iodide, $CH_3\cdot CHI\cdot CH_2\cdot CH_3$, which has been prepared by de Luynes (*Bl.*, ii., 3), who obtained it from erythritol by the action of hydriodic acid, and by Würtz (*Annalen*, clii., 23), by the addition of hydriodic acid to normal butylene. It boils at 117—118°.

Ethyl secondary butyl malonate is formed when this iodide reacts with the sodium derivative of ethyl malonate. It distils at 228—231°, and when hydrolysed yields the corresponding dibasic acid, which on distillation is decomposed, with the formation of *ββ*-methyl ethyl propionic acid, $C_2H_5CH(CH_3)\cdot CH_2\cdot COOH$.

The pure acid boils at 196°, and possesses properties similar to those of the higher fatty acids.

In order to facilitate its identification, the following derivatives were prepared:—

Ethyl salt, $C_5H_{11}\cdot COOC_2H_5$, a colourless oil, boiling at 157—158°.

Anilide, $C_5H_{11}\cdot CO\cdot NH\cdot C_6H_5$, crystallises from light petroleum in silky needles, m. p. 78°.

p-Toluide, $C_5H_{11}\cdot CO\cdot NH\cdot C_7H_7$, melts at 75—76°.

71. "*The Alkaloids of Corydalis cava. Corybulbine.*" By James J. Dobbie, M.A., D.Sc., and Alexander Lauder.

This alkaloid is obtained from the commercial corydaline supplied by Schuchardt of Görlitz, by either of the following methods:—

1. The crude material is dissolved in hydrochloric acid, and the solution mixed with excess of soda, which

throws down the corydaline only. The filtrate is then saturated with carbon dioxide, when the corybulbine separates out.

2. The crude corydaline is repeatedly exhausted with hot alcohol, which dissolves out the greater part of the corydaline. The residue is dissolved in a large quantity of boiling alcohol, from which the corybulbine separates on cooling as an exceedingly fine crystalline powder. It is purified by conversion into the hydrochloride, which, after repeated re-crystallisation from water, is decomposed by ammonia.

Corybulbine is nearly insoluble in water, soluble with difficulty in methyl and in ethyl alcohol, and insoluble, or nearly so, in ether. It dissolves readily in carbon bisulphide, chloroform, and hot benzene. It is also soluble in solutions of the caustic alkalis. An alcoholic solution of the alkaloid rapidly reduces a warm solution of silver nitrate. When heated, corybulbine softens at 210°, but does not melt till 238—240°. A solution of the alkaloid in chloroform is dextro-rotatory.

Corybulbine has the formula $C_{21}H_{25}NO_4$. The hydrochloride, $C_{21}H_{25}NO_4{\cdot}HCl$, is obtained in clusters of prismatic needles by dissolving the alkaloid in hot dilute hydrochloric acid. This salt is remarkable for the difficulty with which it dissolves in water.

The acid sulphate, $C_{21}H_{25}NO_4{\cdot}H_2SO_4$, is prepared in the same manner as the hydrochloride. It dissolves with difficulty in hot water, from which it slowly separates on cooling, in long prismatic crystals.

The platinochloride, $(C_{21}H_{25}NO_4)_2H_2PtCl_6$, is thrown down as a pale yellow precipitate on adding platinum chloride to a solution of the hydrochloride in water containing a little hydrochloric acid.

The methiodide, $C_{21}H_{25}NO_4{\cdot}CH_3I$, a pale yellow crystalline substance, is prepared by digesting the alkaloid with a mixture of absolute alcohol and methyl iodide.

When acted on with a concentrated solution of hydrogen iodide, one molecular proportion of corybulbine gives three molecular proportions of methyl iodide.

72. "*Corydaline.*" Part IV. By JAMES J. DOBBIE, M.A., D.Sc., and ALEXANDER LAUDER.

When subjected to the action of nascent chlorine, corydaline forms a monochloro derivative, $C_{22}H_{28}ClNO_4$, which crystallises from water in flat prismatic crystals.

The specific rotation of corydaline has been found to be +311°.

Oxidation with Potassium Permanganate.—The authors have examined the mother-liquor of corydalinic acid, and have obtained from it several new oxidation products. The mother liquor is neutralised with ammonia and precipitated with lead acetate. On decomposing the lead precipitate with sulphuretted hydrogen and concentrating the solution, a little corydalinic acid first separates out; a mass of crystals then slowly deposits which consists chiefly of hemipinic acid identical with that obtained from narcotine, mixed with a small quantity of a nitrogenous acid which has not yet been investigated. The mother-liquor filtered from the lead precipitate slowly deposits crystals of a neutral substance having the formula $C_{11}H_{13}NO_3$, which contains two methoxy-groups, and is probably an oxy-derivative of dimethoxy-isoquinoline.

The further investigation of the action of hydrogen iodide on corydalinic acid has shown that the chief product of decomposition is protocatechuic acid.

The authors conclude from the results which they have obtained that corydalinic acid, $C_{11}H_5N(OCH_3)_4(COOH)_4$, contains both a benzene and a pyridine ring; that by the action of hydrogen iodide the benzene ring is split off in the form of pyrocatechuic acid, whilst the nitrogenous ring is broken up into ammonia and the non-nitrogenous corydalic acid described in a former paper. The appearance of hemipinic acid amongst the products of the oxidation of corydaline would be accounted for by the oxidation of the benzene ring of corydalinic acid. The analysis of the neutral compound shows that two of the methoxy-groups are attached to the pyridine ring of corydalinic acid. It is therefore probable that corydaline is an alkaloid of same type as papaverine, narcotine, and hydrastine, containing an isoquinoline and a benzene nucleus, but of simpler constitution than these alkaloids, inasmuch as the two nuclei appear to be united directly to one another and not through an intervening carbon atom.

73. "*Attempts to Estimate Sulphur Compounds in the Atmosphere.*" By WILLIAM H. OATES, 1851 Exhibition Science Scholar, Firth College, Sheffield.

The paper contains an account of attempts made to estimate the total amount of sulphur compounds present in the atmosphere of Sheffield.

Various forms of apparatus and different oxidising agents, such as hydrogen peroxide, sodium peroxide, iodine, and potassium permanganate, were tried, but in none of the experiments was it conclusively proved that all the sulphur compounds present in the air were oxidised and retained by the apparatus used.

The results of the determinations tend to show that the amounts of sulphur compounds present in the air, which have been previously published, are considerably too low, and that none of the forms of apparatus used in the experiments described are capable of yielding correct results.

THE ROYAL SOCIETY.

Anniversary Meeting, November 30th, 1894.

The Lord KELVIN, D.C.L., LL.D., President, in the Chair.

THE report of the Auditors of the Treasurer's accounts, on the part of the Society, was read. The Secretary read the list of Fellows elected and deceased since the last Anniversary.

The President then delivered the Anniversary Address, as follows:—

Science has lost severely during the past year. In the list of Fellows deceased, which I have read to you, you have heard the names of Tyndall, Milnes Marshall, Van Beneden, Pengelly, Brown-Séquard, Romanes, Alder Wright, Helmholtz, Marignac, Topley, all well known to you as having been in their lives zealous and successful scientific investigators, who have largely contributed to the object for which the Royal Society works, "The Increase of Natural Knowledge." Tyndall, full of fire and enthusiasm in solid experimental work advancing the boundaries of science, contributed largely, by his brilliant lectures and books, to make science popular, as it now is in England end America. By the sad death of Milnes Marshall on Scawfell, in Cumberland, on the last day of 1893, we lost a young, able, and enthusiastic worker in zoology. A few months later we lost the veteran Pengelly, who did so much for geological science, and gave such delightful and valuable lessons to the larger world of not scientific geologists, in what he did in his exploration of Kent's Cavern, Torquay. Romanes, full of zeal, fighting to the end with the most difficult problems that have ever occupied the mind of man, and devoting his health and his wealth to promote not merely philosophical speculation but also the experimental research by which alone philosophy can have a foundation, left us at the early age of forty-six.

A year ago, in my anniversary address, I called your attention to Hertz's experimental demonstration of electric waves, which he found in working out an experimental problem originally proposed by Helmholtz to him when he was engaged in experimental researches in the Physical Institute of Berlin in 1879. An English translation by Jones, of Hertz's book describing his work on electric waves, dedicated "with gratitude" to Helmholtz, was published in England and America in December, 1893. On the first day of the new year the disciple died, and

within the year the master followed him. Of the whole of Helmholtz's great and splendid work in physiology, physics, and mathematics, I doubt whether any one man may be qualified to speak with the power which knowledge and understanding can give; but we can all appreciate, to some degree, the vast services which he has rendered to biology by the application of his mathematical genius and highly trained capacity for experimental research to physiological investigation.

In his interesting autobiographical sketch he tells us that his early natural inclination was for physics, which he found more attractive than purely geometrical and algebraic studies; but his father could only give him the opportunity of studying physics by his learning medicine to earn a livelihood, and he himself was by no means averse to thus entering on the study of living matter instead of confining himself to the physics of dead matter. I think we may now feel that the world has gained largely by this early necessity for a young man of great genius and power to choose a practical profession.

One early result was his careful examination, while still a student, of the theory of animal heat, and a little later (1847) his great essay, "Ueber die Erhaltung der Kraft," Conservation of Energy as we now call it, communicated to the Society of Berlin on July 3, 1847, of which he said in 1891, "My aim was merely to give a critical investigation and arrangement of the facts for the benefit of physiologists." As a student he had found that Stahl's theory, ascribing to every living body the possession of the property of "The Perpetual Motion" as an essence of its "vital force," was still held by most physiologists." His essay on the "Conservation of Energy," giving strong reasons for rejecting that theory, though looked upon, at first, by many of the physical and philosophical authorities of the time as a fantastic speculation, was enthusiastically welcomed by younger student philosophers, and must soon have convinced the elder men that, whatever may be the real efficiency of vitality, vast and wonderful as it is, it does *not* include the performance of work without drawing upon a source of energy. This conclusion had been virtually foreseen before the end of last century by Rumford and Davy, and had been clearly stated and powerfully supported by Joule and Mayer a few years before Helmholtz found it for himself and successfully persuaded others of its truth.

It is interesting for us now to know that, while thus contributing so effectively to the abandonment of the old doctrine that vital "force" can work without drawing on an external source of energy, Helmholtz was even more effectively concerned in the establishment of a new doctrine which has given a vast extension to the province of life previously perhaps undreamt of, but now universally recognised as thoroughly well established, and supremely important in modern physiology and medicine. On recovering from a typhus fever in the autumn in 1841, at the age of twenty, the last year of his undergraduate course in the Army Medical School of the Friederich Wilhelm's Institute, he spent the accumulations of his income, which free treatment at the hospital during his illness had left him, in the purchase of a microscope, an instrument then but little used in medical education. He began immediately to use it, and made some important observations on the ganglion cells of invertebrates, which, at the suggestion of his master Johannes Müller, he took as the subject of his inaugural thesis for the doctor's degree, in November, 1842, and which was his first published work (Helmholtz's "Wissenschaftliche Abhandlungen," vol. ii., p. 663). With the same microscope, he observed vibrios in putrefying liquids, which he described in his second published paper (1843), "On the Nature of Putrefaction and Fermentation." His distinguished comrade, Schwann, in the laboratory of Johannes Müller, had already shown that vegetable cells are present in fermenting solutions of sugar, and that air, which had been highly heated, was incapable of exciting the fermentation which the access of ordinary atmospheric air was known to produce. Helmholtz found that oxygen, yielded by the decomposition of water in flasks containing small pieces of boiled meat, did not produce putrefaction. Thus the doctrine, held perhaps by all before them, and certainly supported by the great Liebig, that putrefaction and fermentation are purely chemical processes of eremacausis (or slow combustion), produced by oxygen, was thoroughly disproved by the two young investigators. But Helmholtz went farther, and showed almost certainly that the actual presence of a living creature, vibrio, as he called it, bacterium, as we more commonly call it now, is necessary for either fermentation or putrefaction. He proved by experiment that a partition of moist bladder, between the yeast and the fermentable liquid, prevented the entrance of the vibrios which he had observed, *and prevented the fermentation.* It had been reasonably suggested that fermentation or putrefaction might be a purely chemical process produced by a quasi-chemical agent or poison secreted by a living organism; but Helmholtz's observation disproved this supposition almost certainly, because any such chemical substance in solution would pass by diffusion through the bladder, and produce its effect without any direct action of the living creatures. Although Helmholtz himself was characteristically philosophical and conscientious in not claiming as absolutely proved what he had only rendered probable, it is certain that this early work of his on putrefaction and fermentation constituted a very long step towards the great generalisation of Pasteur, adverse to spontaneous generation, and decisive in attributing to living creatures, born from previous living creatures, not only fermentation and putrefaction, but a vast array of the virulent diseases and blights, which had been most destructive to men and the lower animals and crops and fruit. It is well that Helmholtz himself lived to see the great benefits conferred on mankind by Pasteur's work; and by the annulment of the deadliness of compound fractures and the abolition of hospital gangrene in virtue of Lister's antiseptic treatment; and by the sanitary defences against fevers and blights, realised by many other distinguished men as practical applications of the science which his own typhus fever of 1841 helped so much to create.

Close after his work on this subject and on animal heat, followed investigations on the velocity of transmission along the sensory nerves of the disturbance to which sensation is due, the time which the person perceiving the sensation takes to decide what to do in consequence, and the velocity of transmission of his orders along the motor nerves to the muscles which are to carry out his will. Results of the highest scientific interest and of large practical importance were given in two great papers published in 1850 (Helmholtz's "Wissenschaftliche Abhandlungen," p. 763-861.). This was followed a few years later by his "Tonempfindungen," a great work not merely confined to the perception of sound, but including mathematical and experimental investigations on the inanimate external influences concerned in sound, investigation of the anatomical structure of the ear in virtue of which it perceives sound, and applications to the philosophical foundation of the musical art; which holds a unique position in the literature of philosophy, and is certainly a splendid monument to the genius and indomitable working power of its author. Another great work of Helmholtz is his "Physiologische Optik"; who shall say which of the two books is the more important, the more interesting, or the more valuable? Each of them has all these qualities to a wonderfully high degree. Perhaps the most interesting of his experimental investigations in physiological optics was the measurements, by his ophthalmometer, of the curvatures of the several refracting surfaces constituting the lens-system of the eye, from which he ascertained that it is almost altogether by changing the curvature of the front surface of the crystalline lens that the eye is accommodated by its

possessor to vision at different distances. His ophthalmoscope, by which for the first time he himself saw and showed to others the retina of the living eye, was a splendid and precious contribution to medicine. By allowing that outlying portion of the brain to be distinctly seen and examined, it has shown the cause of many illnesses which had been regarded as hopelessly obscure; and for diagnosis and guidance of medical treatment, it is now continually used not only by oculists, but by general practitioners.

Constrained as I feel not to overtax your patience, I find it impossible, on the present occasion, to enter upon Helmholtz's researches in mathematics and mathematical physics farther than just to mention his small but exquisite paper on anomalous dispersion, and the grand contributions to hydrodynamics which we have in his "Integrals of the Hydrodynamical Equations which express Vortex Motion."*

Since our last anniversary, important questions regarding the conduct of the ordinary meetings and the publication of papers, both in the *Transactions* and *Proceedings* of the Royal Society, have been engaging the attention of the Council, with the assistance of a committee appointed on July 5, 1893. The final report of this committee was submitted to the Council on July 5, 1894, when resolutions were adopted accepting some of its recommendations and deferring the consideration of others until after the recess.

At the request of the Royal Geographical Society, a committee was appointed by the Council of the Royal Society to consider the advisability of asking the Government to undertake an Antarctic expedition. A very important and valuable report on the advantages which such an expedition would bring, both to science and to practical navigation, was presented by this committee to the Council on May 24. The Council, after much careful consideration, resolved to ask the Lords of the Admiralty to grant an interview on the subject with representatives of the Royal Society. This request was assented to: and an interview was accordingly held between the First Lord of the Admiralty and representatives of the Royal Society; but the proposal of an Antarctic expedition was not favourably received.

The Joule Fund Committee submitted its report on December 7, 1893, and the Council, on its recommendation, adopted the following resolutions:—

I. That the regulations for administering the Joule-Memorial Fund be as follows:—

1. That the proceeds be applied in the form of a studentship or grant, to be awarded every year, to assist research, especially among younger men, in those branches of physical science more immediately connected with Joule's work.
2. That this grant be international in its character, and awarded alternately in Great Britain and abroad, or in such order as the President and Council shall from time to time decide.
3. That it be awarded in Great Britain by the President and Council of the Royal Society; and, for award in France, offered to the Académie des Sciences, Paris; and in Germany to the K. Akademie der Wissenschaften, Berlin; or in any other country, to the leading scientific institution, for award in that country.
4. That the award in Great Britain be made on the recommendation of a committee, from time to time appointed by the President and Council of the Royal Society, but not of necessity confined to Fellows of the Society.

II. That a sum of £100, which is now, or shortly will be, available, for the first studentship or grant be awarded in accordance with Regulation 4.

The first appointment was accordingly made on June 21, 1894, when it was resolved:—

1. "That a Joule Scholarship of the Royal Society Memorial Fund be awarded to Mr. J. D. Chorlton, of Owens College, Manchester, for the purpose of enabling him to carry on certain researches on lines laid down by Dr. Joule, more especially with the view of determining the constants of some of the instruments employed by Dr. Joule, which can be placed at his disposal by his representatives."
2. "That the value of the Scholarship be £100, payable quarterly, on the certificate from the authorities of Owens College that the researches are being conducted in a satisfactory manner."

On the occasion of Sir George Buchanan's retirement from the post of Chief Medical Officer to the Local Government Board, it was decided by some of his friends that a testimonial should be presented to him, and a sum, amounting to about £340, has been subscribed by medical officers of health, sanitary engineers, and others interested in sanitary science. It was resolved, on the suggestion of of Sir George Buchanan himself, that this testimonial should take the form a medal, to be awarded periodically for work done in connection with sanitary science, and that the Royal Society should be asked to administer the testimonial fund under the following conditions:—

1. The money collected, after paying expenses incurred, to be devoted—
   (*a*) To the foundation of a Gold Medal of the value as nearly as may be of twenty guineas, with a portrait of Sir George Buchanan on the one side and an appropriate design on the other, to be awarded every three or five years in respect of distinguished services to Hygienic Science or Practice, in the direction either of original research or of professional, administrative, or constructive work.
   (*b*) To the bestowal on the recipient of the Medal of the amount (remaining after paying for the Medal and discharging the incidental expenses) which has accumulated since the last award.
2. The Medal to be awarded without limit of nationality or sex.

The Council of the Royal Society has accepted the trust under these conditions; and it was agreed that the first Medal should be given to Lady Buchanan by the testimonialists themselves.

The Catalogue Department has been specially active in the past session. Mr. Ludwig Mond's generous gift of £2000, which I announced to the Society in my anniversary address last year, has given a new impulse to our operations in that department, and enabled us to increase the staff of assistants. Under the able superintendence of Miss Chambers, volume 10 of the Catalogue under author's names has been completed, and was issued in June of the present year. The Society is indebted to several members of the Catalogue Committee who have lent their scientific knowledge to aid in the revision of the proofs, and especially to the Treasurer, under whose experienced eye every sheet in the catalogue has passed. The preparation of copy for a supplementary volume, which will include papers from a large number of periodicals not included in the existing volumes, is now nearing completion.

The Catalogue Committee have held several meetings and discussed some important questions. The proposed subject-index to the existing catalogue has been the chief matter under consideration, and the burning question of the respective merits of an alphabetical and a classified index has been so far settled as to make it possible to commence the work of transcription and translation, nearly 40,000 slips being already finished, so that when the details of the plan agreed upon have been finally settled, as there is good hope they will be in the near future, the preparation of the copy for the printer can be speedily proceeded with. Before, however, any final

* *Philosophical Magazine*, July, 1867, being the translation by Tait of the original German paper, which appeared in *Crelle's Journal* in 1858, and which has been republished in "Wissenschaftliche Abhandlungen," vol. i., pp. 101-134.

steps can be taken, it will be necessary that the supplement volume of the catalogue should have issued from the press. The preparations for this volume are in active progress.

A kindred subject, but one of still wider scope, has been discussed by a special committee appointed by the Council at their first meeting in the present session. The question, namely, of a scientific subject-catalogue, which it is proposed to carry out by means of international co-operation. This committee, with the sanction of the Council, have addressed a circular letter to scientific societies and institutions in this country and abroad, offering by way of preliminary suggestions, first, that the catalogue should commence with the next century; secondly, that a central office or bureau should be maintained by international contributions; and third, that this office should be supplied with all the information necessary for the construction of the catalogue. The circular invites the views on this subject of scientific bodies and scientific men, without in any way committing the Society to farther action. A large number of replies to this circular have been received, many of them carefully prepared and able documents. They will be submitted to the new Council of the Royal Society, and will, I am sure, be most valuable in assisting it to judge as to future proceedings.

The principal question which the Library Committee have had before them during the past session is the accumulation of the stock of *Philosophical Transactions* from the beginning of the century to the present time. New racks have been erected in the basement, which have partly relieved the pressure on our space, but the Committee recognise the necessity of some active measures being taken to increase the sale of this accumulated stock. They are of opinion that the sale might be much facilitated if the memoirs composing the volumes published in the past were made separately available to the public, as is done with those that are published at the present time. On the advice of the committee, the Council have empowered the Treasurer to treat with one of the leading booksellers with the view of bringing some such arrangement into effect.

The collection of marble busts belonging to the Society, which is of such personal and historical interest to all our Fellows, has received a most important and valuable accession. The sons of our former President, Mr. William Spottiswoode—Messrs. Hugh and Cyril Spottiswoode—have presented to the Society a marble bust of their father, by Woolner, which will find in our apartments a fitting home among the busts of many of our former Presidents and distinguished Fellows, and will hand down to posterity a striking likeness of one who deserved so well of the Society and whose premature desease we all still deplore.

The House and Soirée Committee have discussed the advisability of increasing the accommodation in the tea room, and have presented a report to the Council upon the subject. The Council, while not disagreeing with this report, considered it wiser in the present state of finances, to defer the matter for a time.

A third report of the Water Research Committee has been issued during the present year. It gives the results of further experiments by Prof. Marshall Ward on the "Action of Light on Bacillus Anthracis," and on the "Bacteria of the Thames," and the experiments of Prof. Percy Frankland on the "Behaviour of the Typhoid Bacillus and of the *Bacillus Coli Communis* in Potable Water," the whole filling 242 octavo pages.

Unusually large as was the amount of matter published last year, this year the amount is even larger. In the mathematical and physical section of the *Philosophical Transactions*, seventeen papers have been published, eighteen in the biological section. The two sections together contain, in all, 1992 pages of letterpress, and 112 plates; to which must be added eight or ten papers now passing through the press, and probably to be issued before the close of the year. Of the *Proceedings*, ten numbers have been issued, containing 1026 pages. As a result, the finances of the Society are, I regret to say, in not such a satisfactory condition as could be desired. The cost of the publications, which, last year, was far in excess of what it was in previous years, and of what the Society could really afford, has, in the year 1894, amounted to nearly £3260, or about £90 more than it was in 1893. For lithography and engraving alone £1516 have been paid, as against £977 last year. There is, moreover, an accumulation of printed matter now almost in readiness to be issued, the cost of which has still to be defrayed. To meet this extraordinary expenditure it has been necessary to sell out enough of the Society's funded capital to produce £1000, and rigorous retrenchment will be necessary in order to avoid further loss of provision for continued work in future. While the Council feels the importance of all the publications of the Society being as completely illustrated and as fully detailed as the subjects discussed may require, it is evident that some check must be placed on the extent of the publications, and the best manner of effecting this end is occupying the careful attention of the Council.

The establishment of the Faraday-Davy Research Laboratory, in connection with the Royal Institution, is a splendid benefaction which science has gained during the past year, through the untiring and grand generosity of Mr. Ludwig Mond. The Royal Society interests itself in all work contributing towards the object for which it was founded—the increase of natural knowledge; and while gratefully remembering the assistance so generously given to it in the humble but highly valuable work of cataloguing papers which describe the results of scientific investigations already made, it hails with delight this grand foundation of a practical laboratory, of which the purpose is not the teaching of scientific truths already discovered, but the conquering of fresh provinces from the great region of the unknown in nature.

The greatest scientific event of the past year is, to my mind, undoubtedly the discovery of a new constituent of our atmosphere. If anything could add to the interest which we must all feel in this startling discovery, it is the consideration of the way by which it was found. In his presidential address to Section A of the meeting of the British Association at Southampton in 1882, Lord Rayleigh, after calling attention to Prout's law, according to which the atomic weights of the chemical elements stand in simple relationship to that of hydrogen, said:—"Some chemists have reprobated strongly the importation of *à priori* views into the consideration of the question, and maintain that the only numbers worthy of recognition are the immediate results of experiment. Others, more impressed by the argument that the close approximations to simple numbers cannot be merely fortuitous, and more alive to the inevitable imperfections of our measurements, consider that the experimental evidence against the simple numbers is of a very slender character, balanced, if not outweighed, by the *à priori* argument in favour of simplicity. The subject is eminently one for further experiment; and as it is now engaging the attention of chemists, we may look forward to the settlement of the question by the present generation. The time has, perhaps, come when a re-determination of the densities of the principal gases may be desirable—an undertaking for which I have made some preparations." The arduous work thus commenced in 1882, has been continued for twelve years,* by Rayleigh, with unremitting perseverance. After twelve years of it, a first important part of

* "On the Relative Densities of Hydrogen and Oxygen. Preliminary Notice," by Lord Rayleigh, February 2, 1888. "On the Composition of Water," by Lord Rayleigh, February 26, 1889. "On the relative Densities of Hydrogen and Oxygen. II.," by Lord Rayleigh, February 5, 1892, On the Densities of the principal Gases," by Lord Rayleigh, March 23, 1893. "On an Anomaly encountered in Determinations of the Density of Nitrogen Gas," by Lord Rayleigh, April 19, 1894. All published in the *Proceedings* of the Royal Society.

the object, the determination of the atomic weight of oxygen with all possible accuracy was attained by the comparison,* of Scott's determination of the ratio of the volumes of hydrogen and oxygen in the constitution of water, with Rayleigh's determination of the ratio of the densities. The result was 15·82, which is almost 1 per cent (0·87 per cent) less than the 16, which it would be according to Prout's law. It is very slightly less (¼ per cent) than Dittmar and Henderson's value obtained by an investigation† for which the Graham medal of the Glasgow Philosophical Society was awarded in 1890. Values, not quite so small as these for the atomic weight of Oxygen, have been previously found by Cooke and Richards (15·869) and by Leduc (15·876). There can be no doubt whatever now that the true value is more than ¼ per cent smaller than according to Prout's law, and that in all probability it agrees exceedingly closely with the results obtained by Rayleigh and Scott, and by Dittmar and Henderson. The question of Prout's law being thus so far set at rest, Rayleigh, persevering in the main object which he had promised in 1882, "a re-determination of the densities of the principal gases," attacked nitrogen resolutely and, stimulated by most disturbing and unexpected difficulties in the way of obtaining concordant results for the density of this gas as obtained from different sources, discovered that the gas obtained by taking vapour of water, carbonic acid, and oxygen from common air was denser‡ by 1/230 than nitrogen obtained by chemical processes from nitric oxide or from nitrous oxide, or from ammonium nitrite, thereby rendering it probable that atmospheric air is a mixture of nitrogen, and a small proportion of some unknown and heavier gas. Rayleigh and Ramsay, who happily joined in the work at this stage, have since succeeded in isolating the new gas, both by removing nitrogen from common air by Cavendish's old process of passing electric sparks through it, and taking away the nitrous compounds thus produced by alkaline liquor; and by absorption by metallic magnesium. Thus we have a fresh and most interesting verification of a statement which I took occasion to make in my presidential address to the British Association in 1871,§ "Accurate and minute measurement seems to the non-scientific imagination a less lofty and dignified work than looking for something new. But nearly all the grandest discoveries of science have been but the rewards of accurate measurement and patient long-continued labour in the minute sifting of numerical results." The investigation of the new gas is now being carried on vigorously, and has already led to the wonderful conclusion that the new gas does not combine with any other chemical substance which has hitherto been presented to it. We all wait with impatience for further results of their work; we wish success to it, and we hope that it will give us, before the next anniversary meeting of the Royal Society, much knowledge of the properties, both physical and chemical, of the hitherto unknown and still anonymous fifth constituent of our atmosphere.

(To be continued.)

The Detection of Copper Phyllocyaninate in Preserved Green Vegetables. — A. Tschirch (from a separate work).—The behaviour of the evaporated residue of an alcoholic vegetable extract with hydrochloric acid shows whether copper phyllocyaninate is present in a green vegetable product or not. Unmodified chlorophyll when treated with concentrated hydrochloric acid, a deep blue solution of phyllocyanine and a residue which dissolves in either with a yellowish brown colour. If copper phyllocyaninate is present the hydrochloric acid takes up little of a yellow substance, and the residue dissolves in alcohol with a green colour.—*Zeitschr. Anal. Chemie.*

* Scott, "On the Composition of Water by Volume," communicated by Lord Rayleigh, *Roy. Soc. Proc.*, March 23, 1893.

† *Proceedings* of the Philosophical Society of Glasgow, 1890-1891.

‡ "On an Anomaly encountered in Determinations of the Density of Nitrogen Gas," *Roy. Soc. Proc.*, April, 1894.]

§ Republished in Vol. ii., of "Popular Lectures and Addresses."

UNIVERSITY COLLEGE, LONDON, CHEMICAL AND PHYSICAL SOCIETY.

November 28th, 1894.

"*Some Acoustical Experiments.*" By C. V. Burton, D.Sc.

The first of these was designed to render evident the presence of harmonics in the compound tone of a stringed instrument. The note A was stopped on the G string of a violin, and was sounded by bowing in the ordinary way. The presence of the octave-harmonic *a* in the compound tone so produced caused the open *a* string to vibrate, and, owing to the energy expended in maintaining this forced vibration, the harmonic *a* was heard less strongly than it would have been in the natural compound tone of the bowed string. As soon, however, as the open *a* string was lightly touched with one finger so as to stop its vibration, the loss of energy in this direction ceased, and the harmonic *a* was heard with its full intensity. Each time the finger was made to descend lightly on the resonant *a* string and stop its vibration, a sudden increase in the intensity of the harmonic was heard.

In another experiment, two stopped organ pipes, giving the notes *e* and *g*, were connected by flexible tubes with a wind-chest. The apparatus was at some distance from the meeting room, so that the whole body of sound might not be too overpowering, and it was shown that when the pipes, after being held some feet apart, were brought close together, there was a marked increase in the intensity of the difference-tone C_1. This was held to show that the difference-tone has an objective existence, and is generated chiefly in the immediate neighbourhood of the interfering sources of sound. Finally, it was shown that the subjective impression of *pitch* depends not only on the frequency, but also on the intensity of the sound which reaches the ear.

A large tuning-fork, giving the note C, was mounted on a resonance-box, and was made to vibrate strongly by bowing. When the mouth of the resonator was partially obstructed, so as to diminish the intensity of the issuing sound, an apparent *rise* of pitch was noticed, and the subjective lowering of pitch due to great intensity was still more marked when the ear of the observer was brought opposite the opening of the resonance-box at a distance of a few inches in front of it. The effect is more conspicuous with notes of low than with those of high pitch.

A Contribution to the Quantitative Determination of Hydrocyanic Acid.—Georg Gregor. — The gravimetric determination of hydrocyanic acid in officinal solutions should be undertaken by mixing in a stoppered bottle 50 c.c. of the liquid in question with 5 c.c. of ammonia, and after agitation adding at once from 25 to 30 c.c. of decinormal solution of silver nitrate in excess, and after further stirring a suitable quantity of nitric acid, until a slight acid reaction is perceptible. The several operations must be performed in rapid succession without loss of time. It is conveniently diluted with distilled water to about 200—300 c.c., the precipitate is collected on a filter, and the cyanogen is determined by weighing the metallic silver. Of all the known volumetric methods, that of Volhard is the most accurate. He mixes in a ¼ litre flask 100 c.c. of the liquid with 5 c.c. ammonia, 50 c.c. of decinormal silver nitrate, and the necessary quantity of nitric acid free from nitrous acid for slight acidulation, and then adds distilled water up to the mark. After thorough agitation the silver cyanide is allowed to deposit and filtered through a dry folded filter into a dry vessel; 50 c.c. of the filtrate after the addition of a few drops of ferric sulphate are titrated back with decinormal potassium sulphocyanide. The first drop of the sulphocyanide solution must not produce characteristic reddening, otherwise the quantity of silver nitrate added has been insufficient, and the hydrocyanic acid has not been completely precipitated.—*Zeitsch. Anal. Chemie.*

CORRESPONDENCE.

S.T.R. OF OILS.

To the Editor of the Chemical News.

Sir,—In the Chemical News of November 16th (vol. lxx., p. 244), we have noticed a paper, or abstract of a paper, on "Sulphonation of Oils," by Mr. S. G. Hall, in which some statements are made to which attention ought to be called, as Mr. Hall appears to have altered our method of determining the S.T.R. of oils, and yet at the same time adopted our figures without acknowledgment. Mr. Hall states that "it was found that 25 grms. of oil and 5 grms. of 97 per cent acid were convenient amounts to take. These were placed in a glass cylinder and shaken vigorously for a few seconds; the maximum temperature reached was then compared with that obtained with the same amount of acid and 25 grms. of water." Our method of procedure, as described in the *Journ. Soc. Chem. Ind.* for 1891, p. 233, and as given in the late Dr. Alder Wright's standard work on "Oils, Fats, Waxes, and their Manufactured Products," is to treat 50 grms. of the oil with 10 c.c. of sulphuric acid in practically the same way as recommended originally by Maumené, using half these quantities if enough of the oil cannot be secured, and stirring vigorously with a thermometer while the acid is being added to the oil during a limited time, as well as observing certain other precautions. In order to calculate the S.T.R. of the oil 50 grms. of water and 10 c.c. of the sulphuric acid are mixed together in a similar way, and the maximum temperature reached observed as before. It will thus be seen that Mr. Hall employs only 5 grms. of sulphuric acid where we employ 5 c.c., or fully 9 grms., for 25 grms. of the water or oil. Of course it is open to any chemist to alter a published method of analysis, but reasons should surely be given for departing from the recognised process, as so much depends on chemists working in the same way, and especially with the same proportions of oil and acid, in order to obtain comparable results. But this alteration of quantities and method of procedure is not all, for Mr. Hall states, in the table given in his paper, that the rise in temperature when water is mixed with sulphuric acid (presumably with the quantities of each he recommends) is 38·6°, which is precisely the figure we gave originally for the totally different quantities we used. This, to say the least, is a very peculiar coincidence, and comment upon it is useless, especially when it is considered that the figures for the various oils in Mr. Hall's table generally correspond with ours, and, where they do not, a calculation will show that they are wrong. Thus, for example, 104·8° rise in temperature in linseed oil does not give 270 for S.T.R., but the correct figure is 104·5, as given in the original paper already referred to. Mr. Hall also gives results with 98 per cent sulphuric acid, which practically correspond with our results for 99 per cent acid, except for such differences as that just mentioned.

It is scarcely necessary to say anything further except once more to protest against the alteration of recognised methods of testing, without at the same time giving a new series of figures for the various oils, showing that the modification gives results corresponding with the original method, or supplying a fresh series of "constants" in this portion of oil examination.—We are, &c.,

R. T. Thomson.
Horatio Ballantyne.

City Analyst's Laboratory,
156, Bath Street, Glasgow,
December 4, 1894.

Adoption of the Decimal System in Turkey.—The *Chemiker Zeitung* announces that at the end of February, 1895, the decimal system of weights and measures will be adopted in Turkey.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxix., No. 22, November 26, 1894.

Transition from Propionic Acid to Lactic Acid.—Fernand Gaud.—On operating on 500 grms. of liquid, containing 50 grms. of propylic alcohol distributed in twenty tubes, and heating them with Fehling's liquid to 250° for 200 hours, I obtained about 4 grms. of a first acid and 3·5 grms. of a second, both answering approximately to the formula $C_3H_6O_3$. A cryoscopic experiment showed 88 to 89 as the molecular weight. The study of their chemical properties has enabled me to identify the first acid as the ethylidenolactic acid and the second as ordinary lactic acid.

Ether Salts derived from Active Amylic Alcohol.—Ph. A. Guye and L. Chavanne.—The authors give the formulæ, boiling-points, specific gravities, and polarimetric data of twelve amylic ethers which they have obtained.

The Chlorine, called Organic, of the Gastric Secretion,—H. Lescœur.—The chlorine liberated from the gastric secretion by heat, in the state of hydrochloric acid, and taken as a whole, is capable of precise determinations and seems to have a simple physiological signification. But the distinction between free hydrochloric acid and hydrochloric acid in a feeble combination, and altogether the notion of organic chlorine, is far from having the same simplicity. It will be remarked that the notion of organic chlorine, introduced into the chemistry of urine by the application of the method of Hayern and Winter to its analysis, has disappeared in consequence of the more accurate analyses of Petit and Terreil.

Composition of the Red Pigment of Diemyctylas viresecens.—Dr. A. B. Griffiths.—Living specimens of this small American lizard (in its red stage) have been sent to the author by Dr. Prof. S. H. Gaze, of Cornell University. The formula of the pigment appears to be $C_{20}H_{18}N_2O_7$. The solutions of the pigment do not on spectroscopic examination show characteristic absorption bands. The pigment is soluble in alcohol, ether, benzene, and carbon disulphide, but insoluble in water, the acids, and alkalies. By the prolonged action of boiling hydrochloric acid it is converted into uric acid. Hence it is probably a derivative of uric acid, and is of an excretory nature. The author names it provisionally *diemyctiline*.

On Acid Leathers.—Balland and Maljean.—Leather tanned by rapid processes is apt to retain a quantity of sulphuric acid in spite of subsequent rinsings and steepings. This acidity being very prejudicial in the case of strong leathers applied for industrial or for military purposes, it may be detected as follows:—20 grms. of the sample are divided into two equal parts, each of which is cut up into fine shreds. One of these lots is placed in a capsule and moistened with a solution of 1 per cent of pure potassium carbonate. It is placed in the stove, and when quite dry incinerated, which process takes about two hours. The ash is treated with a slight excess of dilute nitric acid and then diluted with distilled water, so as to have after filtration and washing from 30 to 40 c.c. of liquid. It is precipitated whilst hot with barium chloride, and the barium sulphate obtained is determined in the usual manner. The second portion of leather is placed at once in the stove and desiccated without the addition of potassium carbonate. When the desiccation is complete the loss of weight is noted, so as to show the proportion of water present; it is then ignited and treated as above. The weight of the barium sulphate obtained if subtracted from the weight found in the former case

shows the quantity of sulphuric acid, and is referred to 100 parts of the dried leather.

Influence of Arsenic Acid upon the Vegetation of Algæ.—Raoul Bouilhac.—*Stichococcus bacillaris Nægelii* lives and reproduces itself in mineral solutions containing arsenic acid. Other Algæ besides *Stichococcus* are able to vegetate in nutrient solutions containing arsenic acid. Under these conditions these Algæ are capable of assimilating arsenic acid. The addition of arsenic acid to a nutrient solution free from phosphoric acid causes the Algæ to flourish. In this case the arseniates can be substituted for the phosphates.

Journal fur Praktische Chemie.
New Series, Vol. l., Nos. 9 and 10.

Calorimetric Investigations.—F. Stohmann.—This 32nd paper on the thermic value of glycogen has been drawn up by the author in conjunction with R. Schmidt. The thermic value of glycogen per grm. is 4190·6 cal., that of cellulose being 4185·4, and that of starch 4182·5.

Calorimetric Investigations.—F. Stohmann and H. Langbein.—In this paper the authors consider the thermic value of the isomeric acids of the composition $C_7H_6O_3$ and $C_8H_8O_3$. The authors have already shown the incorrectness of the earlier view that isomers of similar constitution have an identical thermic value. They now enter upon a further examination of the same subject.

On Derivatives of Auramine.—J. Finkh and M. Schwimmer.—This paper extends to close upon 50 pages, and contains nothing which would warrant its insertion *in toto*.

Further Contributions to a Knowledge of the Reduction Products of Solid α-Dichlorcyanethyl.—J. Traeger.—This extensive memoir does not admit of useful abridgment.

On the Atomic Weight of Bismuth.—R. Schneider.—The mean result of the author's six determinations is 208·05 (O=16). He considers that it will be perfectly justifiable to accept the round number 208.

Reuniol, a New Terpene Alcohol.—A. Hesse.—This strangely-named compound is a product of the geranium oil obtained from the French colony, Reunion, formerly known as Bourbon. Its composition is $C_{10}H_{18}O$, its boiling point is 225·5°—226°, its specific gravity (at 20°) is 0·865, and its optical rotation in a stratum of 100 m.m, +1° 45′.

Preparation of Benzoic Anhydride.—A. Deninger.—Whilst benzoyl chloride and dry soda do not act upon each other a brisk reaction sets in if pyridine is added to the mixture. The chloride then passes into benzoic anhydride. In place of pyridine there may be used picoline, quinoline, but not dimethylaniline.

MEETINGS FOR THE WEEK.

MONDAY, 17th.—Society of Arts, 8. (Cantor Lectures). "Modern Developments in Explosives," by Prof. Vivian B. Lewes.
TUESDAY, 18th.—Institute of Civil Engineers, 8.
—— Pathological, 8.30.
WEDNESDAY, 19th.—Society of Arts, 8. "Forestry," by General J. Michael.
—— Meteorological, 7.30.
—— Geological, 8.
—— Microscopical, 8.
THURSDAY, 20th.—Chemical, 8. "An Improved Form of Barometer," by Dr. N. Collie. "The Chemical Constituents of *Piper ovatum*," by Prof. Dunstan, F.R.S., and H. Garnett. "Note on the Active Constituent by the Pellitory of Medicine," by Prof. Dunstan, F.R.S., and H. Garnett. "The Preparation of Adipic Acid," by Dr. W. H. Ince. And other papers.
FRIDAY, 21st.—Quekett Club, 8.

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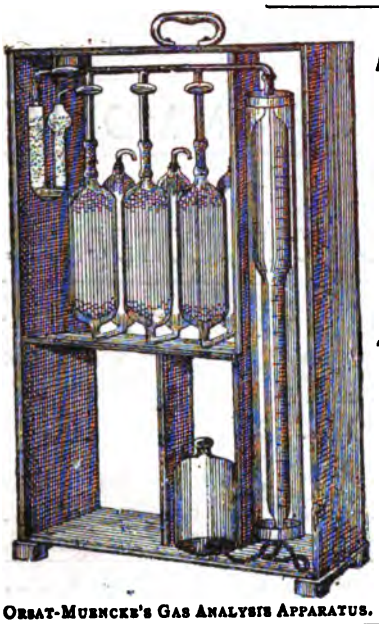

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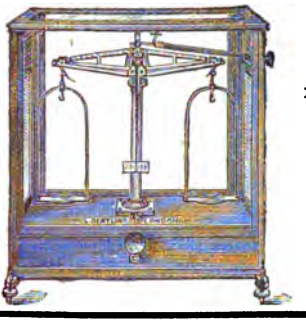

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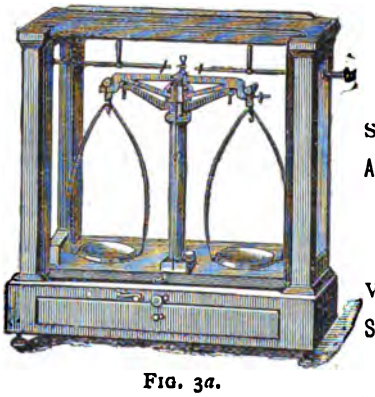

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THE CHEMICAL NEWS.

Vol. LXX., No. 1830.

ALLOTROPS AND ISOMERS.

By C. T. BLANSHARD, M.A.

The data of chemical and physical characters of allotropic forms of elements (allotrops) and isomeric forms of compounds (isomers) are, unfortunately, very defective. I hope, however, by means of a tabular form, to represent the chief known facts about them in such a way that it will be evident that allotrops and isomers are analogous.

Should the data, and the reasoning from them, be sufficient, this will go far to prove that (1), elements are similarly constituted to compounds, especially to organic compounds; (2), certain allotrops and isomers are more evolved than others. The chief literature consulted for this article is as follows:—

Landolt and Börnstein, "Physikalische-Chemische Tabellen," 1894.
Naumann, "Thermochemie," 1882.
Fehling, "Handwörterbuch der Chemie," 1878; vol. iii., "Isomorphism."
E. Petersen, *Zeit. Physik. Chem.* (1891), viii., 601.
H. Debus, *Chem. Soc. Journ.*, liii., 284.
J. W. Retgers, *Zeit. Anorg. Chem.* (1894), v., 211; and (1894), vi., 317.

Element.		Allotrop.	At. vol.	Spec. heat.	Heat of comb. with O.	Heat absorbed.	Cryst. form.	Solubility in CS_2.
P	α	Red metallic.	13·4		—	$P_\gamma = P_\beta$	Hexagonal.	Insol.
	β	Light red.	14·7	} The same	5272	+7100 cals.	Regular?	Insol.
	γ	White.	16·9	} (Regnault).	5747		Regular.	Sol.
As	α	Steel-grey,	13·1	0·0830	1568		Hexagonal.	
	β	Grey am.	15·94	—	1648		Regular?	
	γ	Brown am.	16·0	0·0758	1635		Amorphous.	
S	α	Octahedral.	15·9	0·176	710·8	$S_\beta = S_\gamma$	Rhombic.	Sol.
	β	Prismatic.	16·4	0·232	717·2	$= S_\alpha +$	Monoclinic.	Sol.
	γ	Plastic.	17·1	—	719·9	80 cals.	Amorphous.	Insol.
Se	α	Crystalline.	16·5	—	558·2		?	Insol.
	β	Monoclinic.	17·7	0·0840	562·0		Monoclinic.	Sol.
	γ	Amorphous.	18·4	0·0953	572·5		Amorphous.	Sol.
C	α	Diamond.	3·4	0·1469	938·9		Regular.	
	β	Graphite.	5·3	0·2019	933·6		Hexagonal.	
	γ	Charcoal.	6·8	0·2415	967·0		Amorphous.	

Thomsen ("Thermochemische Untersuchungen," ii., 282) was the first to observe, by a study of the allotrops of S, Se, P, and C, that when a substance gives off heat by its allotropic change, the new substance has a greater density (therefore a less atomic volume) and a smaller specific heat than the original substance.

Let us see if this is also the case with isomers. Inorganic bodies supply but few data.

	Sp. grav.	Heat absorbed.
As_2O_3—		
α crystalline	4·0	$\beta = \alpha + 1200$ cals.
β vitreous	3·71	
$CaCO_3$—		
α aragonite (rhombic) ..	2·94	$\beta = \alpha + 4000$ cals.
β calcite (hexagonal) ..	2·71	

In these tables the lettering of the varieties is made to correspond with a gradual increase of atomic volume, and is therefore more methodical than the arbitrary system in general use.

Thus, by calling white phosphorus γ instead of α, as usually done, the analogy to arsenic becomes in several respects more apparent; Pα and Asα are both hexagonal, with low atomic volumes.

Next, to take organic isomers, which correspond both to allotrops and to polymorphous inorganic compounds.

A. Naumann (*Ber.*, vii., 173, quoted by Carnelley, *Phil. Mag.*, [5], viii., 375), has shown by numerous instances that in organic isomers, the simpler the chain, (1) the less the atomic volume, (2) the higher the melting- or boiling-point.

I have arranged the examples in the order of their boiling-points, which together with the specific gravities, are taken from Beilstein's "Organische Chemie," 3rd ed., 1893, 4. The specific gravities are taken at 15°.

	Formula.	B. p.	Sp. gr.
Pentane—			
α normalpentane,	$CH_3(CH_2)_3.CH_3$	36°·2	0·634
β 4-methylbutane,	$(CH_3)_2.CH.CH_2.CH_3$	31·0	0·628
γ tetramethylmethane,	$C(CH_4)_4$	9·5	—
Hexane—			
α normalhexane,	$CH_3.(CH_2)_4.CH_3$	68·6	0·663
β 3-ethylbutane	$(CH_3.CH_2)_2.CH.CH_3$ ..	64·0	0·676
γ 4-methylpentane,	$CH_3.(CH_2)_2.CH.(CH_3)_2$	62·0	0·701

Similar relations are found to hold with ethers, alcohols, and ketones (*Berichte*, vii., 206).

The further the oxygen is from the centre of the chain, in the cases of ethers and alcohols, the higher the boiling-point.

	Formula.	B. p.	Sp. gr
Ether—			
α methylpropylether,	$CH_3.(CH_2)_2.O.CH_3$	38°·9	0·747
β diethylether,	$CH_3.CH_2.O.CH_2.CH_3$ ..	35·0	0·719
Alcohol, Propyl—			
α normal propylalcohol,	$CH_3.CH_2.CH_2OH$	97·4	0·807
β hydroxypropane,	$CH_3\,CHOH\,CH_3$ ..	82·8	0·788
Alcohol, Butyl—			
α normal butylalcohol,	$CH_3.(CH_2)_2.CH_2OH$	116·9	0·815
β hydroxybutane,	$CH_3.CH_2.CHOH.CH_3$	99·0	0·820

As the melting-points of allotrops are in few cases known with certainty, it will be necessary to employ other data, in order to institute a comparison between these and organic isomers.

Now, T. Carnelley (*Phil. Mag.*, [5], viii., 308) has shown that hardness, melting-point, and atomic volume

are all interdependent; the harder a body is, the higher its melting-point and the less its atomic volume. Let us look at the available data in the table of allotrops. We find that in the case of three elements at least, S, Se, and C, the hardness of the allotrops varies inversely as the specific heat; therefore the melting- (or boiling-) point should vary inversely as the specific heat in these bodies. Again, from the above table the specific heat varies directly as the atomic volume; therefore, for these allotrops, the boiling-point varies inversely as the atomic volume, or directly as the specific gravity, being in complete analogy with the relations found to hold with an immense variety of organic isomers. Thirdly, to take the argument of heat of formation, deduced from heat of combustion. Here, too, we find a complete parallel. Carnelley (*Phil. Mag.*, [5], xiii., 182) has shown that of two isomeric organic substances, (1) the stability, and therefore the heat of formation, of symmetrical compounds (such as we have seen above to have the highest melting-points) is greater than that of asymmetrical compounds isomeric with them; and (2), dependent on the truth of the above, the heats of combustion of the isomers with high melting-points are less than the heats of combustion of those with low melting-points. That is to say, in organic isomers the heat of combustion varies inversely with the melting-point.

So in the organic isomers we have these three relations holding—

$$\text{atomic volume} \propto \text{heat of combustion} \propto \frac{1}{\text{B. P.}}$$

all of which relations hold with the allotrops of the elements.

There are not sufficient data of specific heats of isomers; neither does crystalline form nor solubility of allotrops appear to lead to any consistent results. As far, however, as available data go, both organic and inorganic isomers are found to be exactly analogous to allotrops of the elements.

THE FURFUROSES AND FURFUROSANS.

A Suggestion in Nomenclature.

By C. F. CROSS.

The modern literature of the carbohydrates contains abundant references to the "furfural yielding carbohydrates," and writers are in need of a short descriptive term of general and sufficiently neutral character to include those which have been and remain to be discovered. The purpose of this commmnication is merely to suggest the term *furfurose* as a convenient short description of an aldose which yields furfural under the now generally recognised standard conditions of condensation, and *furfurosan* for the corresponding anhydroforms of such aldoses. The adoption of these shorter designations will avoid the tedious repetition of the present phrase-descriptions.

In the cases of furfural yielding compounds, not aldoses, but containing also the COOH group, *e.g.*, glycuronic acid, the above terms would not strictly apply. As, however, the necessity for such general descriptions arises in the case of complexes met with in plant tissues, *e.g.*, celluloses, oxycelluloses, and lignocelluloses, and not in the case of isolated compounds of known composition and configuration, the term might still apply with the extended definition "Aldoses or their immediate derivatives which yield furfural as the characteristic product of decomposition by condensing acids."

This preliminary suggestion is made to elicit any criticisms which may occur to specialists, in absence of which the term will be used in forthcoming publications on which the writer is engaged.

ARGON.

The Newly Discovered Gaseous Constituent of the Atmosphere.

At the last meeting of the Royal Society it was announced that a paper by Lord Rayleigh and Professor Ramsay on the New Gas, to which the name of Argon* has been provisionally given, will be taken as the subject of discussion at the meeting on January 31st, 1895. This will be the first meeting under a resolution of the Council, passed last session, whereby certain meetings—not more than four in each session—will be devoted each to the hearing and discussion of some one important communication.

LONDON WATER SUPPLY.

Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending November 30th, 1894.

By WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To Major-General A. De Courcy Scott, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, December 10th, 1894.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from November 1st to November 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 182 samples examined, sixteen were recorded as "clear but dull," and only one as "slightly turbid." In case this record may appear more serious than it really is, we may explain that this means "slightly turbid" when examined in a stratum two feet thick. To an ordinary consumer, looking at the water in a carafe or tumbler, it would not appear different from those we have recorded as "clear and bright." The suspended matter is of a harmless, inorganic nature.

The floods in the Thames valley during the month of November have been the severest since the year 1821, and it was not to be expected that the water supplied from the river would not show some signs of the flood. The average rainfall at Oxford during November is 2·31 inches, while the actual rain has amounted to no less than 4·8 inches, showing an excess of 2·49 inches. There is one striking peculiarity connected with the rainfall during November. In most exceptionally wet seasons the fall of rain is more or less evenly distributed over the month. The month which has just closed had, however, seventeen days on which no rain fell, and eight other days on each of which less than 2-10ths fell. On the remaining five days—the 7th, 11th, 12th, 13th, and 14th—no less than 4·02 inches fell, while the rest of the month must be called very dry, only 0·17 inch of rain having fallen since the 14th. The sudden downpour of four inches of rain in five days—amounting to 69½ million gallons per square mile—largely overtaxed the capacity

* ἀν-ἔργον; *no work*. Symbol, A.

of the river to carry it off, whereas had this amount been more evenly distributed over two or three weeks no harm would have been done.

Bacteriological examinations of the waters have been carried on unremittingly during the month, for it was important to ascertain day by day how the filter beds of the various companies were working under the unprecedented strain to which they were subjected. This was important in the interests of the public as well as of the companies, for being thus in a position to warn the officials of the first approach of a rise in the number of bacteria, it would be comparatively easy to apply a remedy before the waters could be called bacteriologically impure. Water drawn into sterilised tubes from the pure water reservoirs at the different companies, and then cultivated in nutritive gelatin for forty-eight hours in darkness, gave numbers of colonies ranging from 4 to 70 per c.c. It having been objected that on exceptional occasions it would be more satisfactory to test, bacteriologically, the waters as actually delivered to the public, and drawn from the mains at the same places where the samples for analysis were taken, a series of sterilised tubes were filled at the different standpipes when the other samples were drawn, and these were also examined bacteriologically. The number of colonies yielded per c.c. by the waters from the different companies in no case exceeded the number which would be admissible in a pure drinking water.

It will be observed that in several instances the colour of the waters has been higher than usual. The entire absence of ammonia, and the high ratio between the organic carbon and nitrogen, show, however, that the colouring matter is almost purely of vegetable, peaty origin.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

NOTE ON THE ESTIMATION OF IRON AND ALUMINA IN PHOSPHATES.

By VINCENT EDWARDS, F.C.S.

As the above is an important matter to those engaged in the manufacture of superphosphates, I venture to draw attention to one or two facts which I noticed in some experiments I recently made. Being asked to ascertain the solubility of the phosphoric acid of bone-ash in a neutral solution of ammonium citrate, the usual strength of which is about 20 per cent $Am_3C_6H_5O_7$, I at the same time operated on a sample of Florida phosphate, and the result obtained seems to indicate a short and reliable method of arriving at the amount of iron and alumina, also the percentage of tri-calcium phosphate which will not appear as water "soluble" in the manufactured manure. To begin with, the bone-ash which contained 35·2 per cent P_2O_5 gave 5·85 per cent P_2O_5 soluble in the citrate after half an hour's treatment at 60° C. to 65° C. As the sample was almost free from iron and alumina this P_2O_5 is evidently present as $Ca_2H_2P_2O_8$, a compound not occurring in the ordinary raw phosphates of commerce, and which would not therefore interfere with the short method I would propose for factory work. The Florida phosphate on applying the same treatment gave 3·67 per cent P_2O_5; this is practically the amount in combination, or which would combine with iron and alumina as known by the analysis of the phosphate. This being so might not a chemist engaged in a manure works, on being asked to give some idea as to the amount of iron and alumina present in any sample of mineral phosphate, proceed thus? Take 1 grm. of the well-ground sample, and in a small flask such as is used for Kjeldahl's process, heat with 50 c.c. of citrate at about 60° C. in the water-bath for half an hour, filter and wash; clear up any precipitate or cloud of lime by boiling with the addition of a little nitric acid; cool, and throw down the P_2O_5 with citro-magnesia solution and excess of ammonia; stir well, set aside for two hours; filter, wash, dry, ignite, and weigh. To the filtrate add sulphide of ammonium; warm, collect the precipitate of FeS; wash, dissolve in dilute sulphuric acid; boil, cool, and titrate with permanganate. This could certainly be done in a reasonable time, and would, I think, be found reliable for raw phosphates. In the above the alumina is found by difference, but so it is in the ordinary text-book method, a method which, most excellent as it is, is long and tedious. We have here another proof of the uselessness of citrate for estimating the "available phosphate," as it is evidently absurd to suppose that the phosphates equal the iron and alumina alone are of value when applied direct.

Lawes' Works, Barking.
Dec. 10th, 1894.

THE EVAPORATION OF CARBON.

By HENRI MOISSAN.

In the series of researches which we have carried on by means of the electrical furnace, we have had the opportunity to collect the results of a number of experiments on the evaporation of carbon. We summarise them in this memoir.

Hitherto the formation of carbon vapour had been established only in the electrical arc, either by the aid of spectrum analysis or of the beautiful synthesis of acetylene due to Berthelot. We may demonstrate the existence of this volatilisation, independently of the arc, in the following manner:—

If we place a tube of coke, of an inside diameter of about 1 c.m., in the midst of an electric furnace of quicklime heated by a powerful arc (2000 ampères and 80 volts) we see the interior of the tube becoming rapidly filled by a black, but very light, felting produced by the condensation of the vapour of carbon.

We may further render this vapour of carbon visible by placing in a boat in the midst of the tube, and strongly heated, some crystallised silicon. We then see the silicon melt, enter into ebullition, and as the vapour rises it meets the vapour of carbon descending from the upper part of the tube, and there is produced between the boat and the tube a lace-work of fine needles of carbon silicide. This crystalline and transparent compound is formed by the direct union of the two vapours.

At the very high temperature produced in our electric furnace, we can, therefore, volatilise carbon outside of the arc.

We thought it interesting to study the production of this vapour. In general a substance passes from the solid to the liquid state and then, on a sufficient increase of temperature, it takes the gaseous state. Does carbon behave in the same manner, or does it form an exception to the general rule? The following experiments will decide the question:—

We placed in the interior of our electrical furnace, heated by means of an arc of 1200 ampères and 80 volts, a small crucible of very pure coke, into which the massive lid was introduced deeply by means of gentle rubbing. This small crucible was placed on a disc of coke supported by a bed of compressed magnesia. Heat was applied for ten minutes, and the temperature reached was sufficient to volatilise several hundred grms. of lime and magnesia.

After cooling, the lid, which had remained in its place, did not at all adhere to the crucible; all the mass had been converted into graphite, but the surfaces were not soldered together.

If we place a boat of coke in a tube of the same

material, and if we heat the tube either superficially or from the interior by means of a powerful arc, we never succeed in welding the boat to the tube.

If we cause an arc of 1000 ampères and of 80 to 90 volts to act in our electric tube furnace, it often happens that the upper part of the tube which is the most exposed to the thermic action of the arc is perforated, but the edges of the perforation, after cooling, display no trace of fusion.

We heated charcoal of sugar in a covered crucible by means of an arc of 1000 ampères and 70 volts. The sugar charcoal preserved its form; it still retained the minute holes through which the gaseous hydrocarbons escaped in the course of its formation. It was entirely converted into graphite, but the pulverulent mass if examined under the microscope with a low power presented no trace of fusion.

On heating in the same manner graphite, wood-charcoal, and retort-coke, all purified by means of chlorine, we found after the experiment nothing but graphite, but each variety had retained its form and displayed no trace of fusion or welding.

On examining the electrodes used in these experiments, formed of the purest carbon possible, we found that the points were rounded, completely converted into graphite, but presented no trace of melted matter. With a current of 2200 ampères and 70 volts the transformation of electrodes of 0·05 in diameter was effected for a length of 15 centimetres.

We may even form the extremity of the positive electrode of a cylinder of coke, adjusted by gentle friction, and after the experiment, this cylinder, which has been in the hottest part of the arc, is deformed, but it is not soldered to the electrode.

We must remark that the case is different if the coke employed contains impurities, such as metallic oxides, silica, or boric acid.

We have already indicated that in this case the boric acid yields a definite and crystalline carbon boride of the formula B_6C. This carbon boride may combine with an excess of carbon and produce bodies, apparently fused, of a rounded form, and drops sometimes of very great hardness, but which are not formed of pure carbon. A very small quantity of metallic impurities may in like manner give carbides melted or crystalline, several of which I have described. It is therefore essential to employ in experiments only the purest possible carbon.

According to these experiments, carbon passes from solidity to the gaseous condition without assuming a liquid state.

It remains for us to study the variety of carbon produced by the condensation of this vapour.

We have collected the vapour of carbon by three different procedures:—

1. *By Distillation.*—The vapour of carbon condensed in the coke-tube, as described above, yielded us a black deposit entirely consisting of graphite.

2. *By Condensation upon a Cold Substance.*—When we placed in our electric furnace a tube of copper traversed by a current of cold water we collected on its surface a black deposit which was treated with very dilute hydrochloric acid in order to free it from quicklime. The deposit contains small spheres of silica and other impurities, but it is mainly formed of carbon, the particles of which, heavy or light, are formed of microscopic crystals presenting all the characters of graphite.

3. *By Condensation upon a Hot Surface.*—On causing the electric arc to play into a furnace of quicklime, to avoid the presence of the carbonic acid which absorbs the vapour of carbon and is converted into carbonic oxide, we obtain, especially at the positive pole, fungoid growths of carbon derived from the volatilisation of this substance in the arc itself.

The carbon, the surface of which is more or less rounded, presents on microscopic examination no appearance of fusion. Its specific gravity is 2·10. On analysis it yields, per cent, 99·61 to 99·90 of carbon, and contains only an insignificant trace of ash. It is therefore pure carbon obtained by distillation; it presents all the characters of graphite, and cannot be burnt in oxygen except at a very high temperature, so that its combustion can only be effected in a tube of porcelain.

In fine, all the condensations of the vapour of carbon have always yielded graphite.

When these various experiments had been concluded we thought it desirable to verify them by means of a small well-known apparatus—the glow-lamp. Everyone knows in these days the arrangement of this apparatus. A filament of charcoal is connected to the extremities of two platinum wires by means of an electrolytic deposit of copper. The filament is then enclosed in a glass vessel, in which the air is exhausted by a mercurial pump. After being used for lighting for a time varying from 500 to 900 hours, we see a slight black veil appear on the glass. This deposit increases and soon renders the lamp unfit for use. At other times, if the current is too intense, the filament burns at some one point and gives at the same time, suddenly, the same deposit, which is diffused uniformly over the interior of the glass.

If we collect this black deposit in a glass of water, and examine with the microscope, we remark—very small crystals of carbon silicide of a characteristic form, piled up crystals reminding us of the silicon obtained by Marsden in melted silver, and especially small masses of a black colour more or less agglutinated. This last deposit under a high magnifying power presents no trace of crystallisation. We must remark at the same time that there floats upon the liquid a thin pellicle, which under the microscope appears of a maroon colour. The contents of a lamp were treated with a mixture of nitric acid and potassium chlorate, and the black matter was not at once destroyed. We kept this mixture for twelve hours at the temperature of 60°, and after washing and decantation the slight deposit obtained, on examination with the microscope, displayed very distinct crystals of graphitic oxide. The small upper lamina was then removed, the liquid evaporated, and the residue, still on the same plate of glass, was heated to dull redness. A fresh microscopic examination showed that all the yellow or greenish crystals had disappeared and had been succeeded by a flocculent deposit, much more voluminous. This black deposit disappeared in turn if ignited in air to dull redness. We may conclude from this experiment that the veil formed on glow-lamps is chiefly composed of graphite.

If, on the other hand, we examine with the microscope the ends of the filament which has been ruptured in a glow-lamp, we find that the points of the filament do not appear to have been melted, but that they are taper and bristle with small crystals of graphite.

From all these experiments we may infer that either in a vacuum or at the ordinary atmospheric pressure carbon passes from solidity to the gaseous state without taking a liquid condition. In this respect it may be compared to arsenic.

When gaseous carbon returns to the solid state it always yields graphite.

Still, we are of opinion that carbon may be rendered liquid, but that this phenomenon can be produced only by means of strong pressure. In the case of high pressures, as our former experiments have proved, the density of carbon increases and we obtain diamond. In my ingots of iron refrigerated in lead I have produced small diamonds presenting the appearance of an elongated drop, as it is sometimes met with in nature. We know that there are found at the Cape and in Brazil diamonds possessing no trace of apparent crystallisation, and which have rounded forms like those which a liquid might assume if kept in the midst of a pasty mass. Carbon under pressure might, therefore, take a liquid state and solidify like water, presenting either a confused mass of crystals, or taking a rounded and amorphous figure.—*Comptes Rendus*, cxix., p. 776.

OXIDATION OF THE FORMAZYL COMPOUNDS.

By H. VON. PECHMANN and P. RUNGE.

FORMAZYL compounds yield on oxidation products of quite a different kind from the phenylhydrazones; that is to say, colourless quaternary ammonium bases in which the imide-hydrogen is in the first place oxidised to hydroxyl. The substance thus formed is only an intermediate product. Its constituents are transformed so as to form a ring of members and a pentavalent nitrogen atom. The new substances are to be regarded as derivatives of Bladin's tetrazol, and will therefore be named tetrazolium hydroxides.

The course of the oxidation depends on the nature of the oxidising agent. In the absence of acids there are formed free bases, and, in presence of acids, their salts. By oxidation with mercuric oxide in a chloroform solution, we obtain the chlorides.

The constitution of the new compounds, and their relation to tetrazol, could not hitherto be obtained in the most simple manner.

The new compounds are strong bases which are most readily separated from their chlorides by silver oxide. They are easily soluble in water, but quite insoluble in ether. The colourless aqueous solutions turn turmeric paper brown, absorb carbonic acid, and behave like the fixed alkalis in contact with metallic salts.

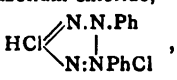
The salts which they form even with weak acids are remarkably stable. They crystallise readily, dissolve in water, are less soluble in alcohol, but insoluble in ether. These salts are colourless except the acid is coloured, but turn yellow on exposure to light. The chlorides give crystalline compounds with platinum chloride, gold chloride, and other metallic salts. Iodised potassium iodide gives dark crystalline iod-addition products.

They are very readily attacked by alkaline reducing agents, especially by ammonium sulphide.

Their physiological action has been examined by Dr. Hildebrand, physician to the Elberfeld Colour Works. The neutralised solution of diphenyltetrazolium chloride carbonester has an emetic action, but diminishes the arterial pressure, and death ensues with symptoms of paralysis of the heart.

The following reactions were obtained with the aqueous solution of diphenyltetrazolium chloride-carbonester:—Potassium bromide, after a time colourless needles of bromide; potassium iodide, yellow crystalline iodide; sodium nitrate, an oily nitrate crystallising in time; sodium nitrite, the same; potassium chromate, a yellow chromate; picric acid, a yellow picrate.

The diphenyltetrazolium chloride,—



crystallises in shining needles grouped in stars; melts, with decomposition, at 268°; soluble only in water, alcohol, and acetone.

The aqueous solution behaves with salts as follows:—Potassium bromide, sodium carbonate, no precipitate; sodium nitrate, nitrite, sulphate, and phosphate, and potassium chromate give sooner or later crystalline precipitates. Potassium iodide, an immediate yellow precipitate; permanganate, a violet; picric acid, a yellow. Iodised potassium iodide throws down an iodised addition product, crystallising from alcohol in brown leaflets with a violet reflection, and melting at 167°. Silver oxide deposits silver chloride, and gives a colourless alkaline solution of the free base which with metallic salts behaves like the fixed alkalis. The alcoholic solution of the chloride coloured red by alcoholic potassa.

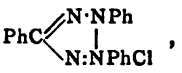
The chloro-platinate is thrown down as a flesh-coloured amorphous precipitate, which crystallises from hot water in orange-yellow prisms.

The chloraurate is a golden yellow precipitate crystallising from alcohol in prisms, and melting at 209°, with decomposition.

The iodide is a yellow precipitate, melting with decomposition at 237°.

The nitrate crystallises from alcohol-ether in colourless needles.

Triphenyltetrazolium chloride,—



forms colourless shining needles from alcohol-ether, but from boiling chloroform it separates in needles of a satiny lustre, containing one mol. chloroform; turns yellow in light; melts, with decomposition, at 243°; soluble in water, alcohol, and acetone. The watery solution yields the following precipitates:—With potassium iodide, yellow; with sodium carbonate, white, crystalline; with sodium nitrate, an oily salt which soon crystallises; with sodium nitrite, colourless needles; with potassium sulphate, a sulphate which crystallises after some time; potassium chromate, a yellow chromate; potassium permanganate, a violet precipitate; picric acid, a yellow picrate; iodised potassium iodide, a dark addition-product, which crystallises from alcohol in prisms nearly black, but transmitting a reddish light. Melts, with decomposition, at 137·5°. Formazylbenzol is reduced by ammonium sulphide. A plate of zinc in the neutral or acetic solution is covered with a red coating of formazylbenzol. The chloroplatinate forms yellow leaflets fusible at 237°.—*Berichte*, xxvii., No. 16, p. 2920.

GERMAN PRE-EMINENCE IN CHEMICAL MANUFACTURES.

PROF. W. OSTWALD, writing in the *Zeitschrift für Physikalische Chemie*, states that some years ago he accidentally read that so-and-so many thousand cwts. of benzene, the chief part of the total national produce, were yearly exported from England to Germany. In itself this is only one number among many, but if such numbers are allowed to speak they may tell us much. Benzene is not used as such; it serves for conversion into other substances, dyes, scents, medicines, &c. It is therefore an intermediate product, and we see here the remarkable spectacle that the oldest industrial country is compelled in the conversion of coal-tar into the products above named to stop half-way and leave the most important and lucrative part of the manufacture to another nation. Further, England was the first country which undertook the manufacture of the benzene dyes on a large scale. What, therefore, are the causes which have led to this strange displacement? I found the answer on visiting England and studying the local conditions more closely.

In an important industrial city I visited a colleague who teaches chemistry in a local college. He showed me with pride his laboratory, which was in fact very beautifully equipped. But then followed the unavoidable query, "How many working students have you?" I will not here mention the number, but it was remarkably small in comparison with the total of students in the college. "Yes," said the professor, "my colleague on the other side has five times as many." It appeared that this other professor taught in his laboratory, not chemistry, but dyeing and tissue printing, and had consequently a great number of pupils. The young future technicist in England is too "practical" to study chemistry in its abstract form. If he intends subsequently to enter dye works he studies dyeing. In Germany this is inverted; there every future technical chemist studies above all things chemistry; its applications follow afterwards. The necessary result is that the English technicist must begin afresh if there occurs any important altera-

tion in his department. The German falls back upon the general principles which he has assimilated, and is quickly at home.

There is no sphere in which the superiority of our educational practice is shown so brilliantly as in technical chemistry. The laboratory of a chemical works that is on a level with the present day differs from that of a University only in being better equipped, and the researches there carried out are a direct continuation of the scientific investigations conducted at the University. This is the secret of the success of German Industrial chemistry, the recognition that science is the best practice.

Professor Ostwald sees one part of the evil, but not the whole. He had not the opportunity to observe how the time and the brain-power of the English student are frittered away in preparing for examinations, and how the English professor is fettered by some syllabus which prevents him from teaching according to his own judgment. Nor could he see how the English manufacturer is hampered by our faulty patent-laws.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 6th, 1894.

Dr. Armstrong, President, in the Chair.

Professor P. T. Cleve, of Upsala, Foreign Member of the Society, was present at the meeting, and signed the Roll of Fellows.

Messrs. Arthur P. Hope, William F. Mawer, E. C. Thompson, and Arthur Ross were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. David Butler Butler, 41, Old Queen Street, Westminster, S.W.; Tom Crossman, 40, Coldhurst Street, Oldham; Frederick Weldon Daw, Bishop's Road, Ebbw Vale, Mon.; Weldon Hanson, 30, Baker Street, Middlesbro'-on-Tees; Walter Harris, B.A., Ph.D., Campbell College, Belfast; Hugh Hastings, 10, Yew Tree Road, Kidderminster; James Albert Offord, 46, St. Giles Street, Norwich; Thomas Chilwell Sharrott, Grendon Lodge, Atherstone; David John Williams, Ty Newydd Farm, Garn Dolbenmaen, Carnarvon; Evan Williams, Rochdale Road Gas Works, Manchester.

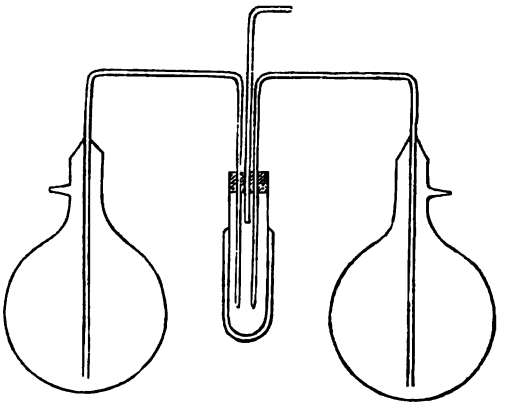
The following were duly elected Fellows of the Society:—Messrs. Frederick John Allen; George H. Allibon; John Allport, M.A.; Stéphane Barlet, B. ès Sc.; Henry Spencer Blackmore; D. R. Boyd, B.Sc.; John Samuel Strafford Brame; James Bruce; George William Burman; William Bush; Alexander Cameron; Ezra Catherall; Joseph F. Chambers; Arthur Herbert Coote; William Michael Doherty; Cecil Cooke Duncan; Frederic Dunn; Lewis Benjamin Saltwell Dutson; Charles A. Fogg; Donald Gordon Forbes; Alfred Greeves; John Hall; Edward Haworth, B.Sc.; Albert Helms, Ph.D.; Martin Stanger Higgs; Alexander Frederick Hogg, M.A.; George Cecil Jones; James Knight, M.A., B.Sc.; Richard S. Ladell; Bevan Lean, B.A., D.Sc. (Lond.); W. H. Lewis, B.A.; George William MacDonald, B.Sc.; Charles James Shaw Makin; James McCutcheon; Thomas Omerod; Gerald G. Quinn; David Gibson Riddick; Alfred George Scorer; Claude Smith; Albert Taylor; Cuthbert Vaux; William G. Wagner; William L. Warren; Robert Waterhouse; Christopher Wilson; Robert Hanbury Wilson; Alexander Poole Wilson; James Young.

Professor Dewar exhibited a vacuum-jacketted globe containing about half a litre of liquid air, which had been kept for the previous thirty hours at the Royal Institution.

Of the following papers those marked * were read:—

*74. "*The Relative Behaviour of Chemically Prepared and of Atmospheric Nitrogen in the Liquid State.*" By James Dewar, F.R.S.

When gases such as nitrogen, oxygen, or air are liquefied in large quantities, the impurities found in the gases and taken up during the passage through the pumps gradually accumulate, and when the fluids are discharged into vacuum vessels at atmospheric pressure these separate in the solid state. If the solid matter is filtered off from liquid air and the fluid allowed to evaporate slowly from a vacuum vessel, then the last drops of liquid are almost pure oxygen; nitrogen gas containing 3 or 4 per cent of oxygen when liquefied behaves exactly in the same way. It would appear, therefore, that no impurity of higher boiling-point than oxygen can be separated by ordinary fractional distillation of the liquid air, and if any other material is present it must evaporate along with the nitrogen. By the use of a special arrangement small quantities of gases, in a pure and dry state, amounting to from 100 c.c. to a few litres, may be examined in the liquid condition and the experiment repeated as often as desired with the same specimen of gas.



The simple apparatus exhibited, by means of which the condensing-point of a gas and afterwards the volatilising rate of the resulting liquid may be observed, may be sufficiently described as follows:—A tube of small bore, somewhat drawn out at one extremity, is passed nearly to the bottom of a distillation flask and sealed into the neck. The outer portion of this tube is closed and bent twice at right-angles, so that a closed limb is thus formed outside the vessel. The side tube of the flask is sealed after the pure dry gas under examination has been introduced together with phosphorus pentoxide, at a known pressure and temperature. The closed limb of the small-bore tube is then cautiously introduced into a vacuum-jacketted tube containing liquid air or oxygen, so arranged that the vapour-pressure on the liquid may be gradually lowered by means of an air-pump, and the gas within the tube slowly reduced to the temperature of liquefaction. In this way it is easy to observe the point at which liquid begins to form from different samples of gas placed side by side, and afterwards, when the temperature of the liquid air bath is allowed to rise, the point at which the last drops of the liquids resume the gaseous form. Nitrogen obtained from atmospheric air has been compared in this manner with nitrogen prepared from nitric oxide without any differences between them being detected. Atmospheric nitrogen which has been passed over heated magnesium showed, however, a marked difference as compared with gas which had not been so treated. Although its condensing-point was not far removed from that of the untreated material, as a matter of fact this point, as well as the volatilising-point of the resulting

liquid, was higher than before; that is to say, nitrogen which has been passed over heated magnesium becomes liquid a little before the original specimen, and the liquid evaporates rather more slowly and lasts longer when both substances are compared under precisely similar circumstances. Nitrogen chemically prepared from nitric oxide was likewise changed by passing it over heated magnesium, for after this operation it liquefied and evaporated at a rather higher temperature than previously.

It would, therefore, appear that, whilst atmospheric nitrogen does experience change when passed over heated magnesium, some effect is also produced on chemically prepared nitrogen; and, as far as these experiments have been carried, they reveal no very marked difference between the behaviour of nitrogen from atmospheric air and nitrogen obtained from its compounds by chemical methods. It may be, however, that any concentrated impurity boils nearly at the same temperature as the original nitrogen, or that the amount present is so small that it does not liquefy at the temperature of $-200°$ C. Considering that the flasks of 150 c.c. capacity contained the concentrated impurity of 10 litres of nitrogen, the partial pressure of small quantities of other matter ought to be very considerable, so that we might anticipate liquefaction at $-200°$ C. At the lowest temperature reached, atmospheric nitrogen which had been passed once over magnesium gave clear transparent crystals along with liquid, while the untreated nitrogen remained fluid. All the samples of nitrogen and oxygen properly purified, when liquefied in the above manner, are clear transparent liquids, so that the solid matter which always separates when air or nitrogen or oxygen is liquefied on the large scale consists of impurities. If a manometer is attached to the flask containing the gas, and at the same time the condensing tube is calibrated, the method of working gives quantitative results, since the pressure in the flask and the volume of liquid condensed can be simultaneously observed.

Further, if we use liquid oxygen as the cooling agent we can observe the vapour pressures of two or more substances at the same temperature, and these pressures may be expressed in terms of the vapour pressure of oxygen. In this way all very volatile liquids would be comparable with oxygen as a standard. If the vapour pressures of the substances are known with sufficient accuracy then the pressure in the flask which has been supplying the gas for liquefaction can be calculated. The following formulæ are sufficiently accurate, where N and O are respectively nitrogen and oxygen pressures in centimetres of mercury, and T absolute temperature.

$$\text{Log. N} = 9{\cdot}0762 - \frac{583{\cdot}8}{T}$$

$$\text{Log. O} = 8{\cdot}5681 - \frac{616{\cdot}8}{T}$$

therefore—

$$\text{Log.}\frac{N}{O} = 0{\cdot}5081 + \frac{33}{T}$$

According to the formulæ, if the oxygen bath is reduced to 2 c.m. pressure, the pressure in the nitrogen flask is 17·8 c.m., so that nearly three-fourths of the original mass of gas filling the flask appears in the liquid state. At the same time it must be understood that these experiments are merely qualitative, and were not carried out with the view of separating any new substance from air or nitrogen. Their chief object is to observe the points of condensation and evaporation of gases liquefying between $-180°$ C. and $-200°$ C. at and below atmospheric pressure.

Small amounts of known impurities cause marked differences in the amount of liquid formed from the same volume of gas similarly treated. Thus a trace of impurity, presumably hydrogen, in a sample of nitrogen subjected to liquefaction in the above manner only gave one-third the volume of liquid that a similar flask gave when filled with pure nitrogen. This is due to the concentration of the hydrogen or other non-liquefiable material in the narrow tube where liquefaction takes place.

This plan of working may be conveniently applied to testing whether the oxygen and nitrogen in air liquefy simultaneously. Such a question cannot be answered by liquefying air under pressure. If, however, two flasks such as have been described are taken, one filled with nitrogen at 0·79 of the atmospheric pressure, and the other with oxygen at 0·21 of the atmospheric pressure (the temperatures being equal), then on cooling them side by side the instant at which liquefaction takes place in the narrow condensing tubes can be observed. The oxygen always appears a few seconds before the nitrogen, and remains after the latter has evaporated. The boiling-points of nitrogen and oxygen, under the respective pressures at which they exist in the atmosphere, are very close together.

Discussion.

The President, referring to experiments on the liquefaction of gases which he had recently witnessed in the Royal Institution Laboratory, said that the means of producing very low temperatures during long periods, now at Professor Dewar's disposal there, were marvellously complete, and important results ought, before long, to flow from their application.

It was useless to deny that special interest attached to the communication to which they had just listened, but, unfortunately, in the absence of Lord Rayleigh and Professor Ramsay, they were left in the position of having to play "Hamlet" with only the ghost present, and, under such circumstances, the play obviously could not be continued to a successful issue. Chemists were deeply interested by the statements relating to the discovery of a new constituent of the atmosphere, brought before the British Association at Oxford, but they awaited further information before making up their minds. They were in a very different position, however, since Friday last, when the President of the Royal Society, in his address, referred to this discovery as the greatest scientific event of the year. It was to be supposed that the President of the Royal Society had information at his disposal, not hitherto made public, which justified so definite a statement, and naturally chemists would impatiently await its disclosure. He ventured to say that Lord Rayleigh and Professor Ramsay now could not hope to keep so remarkable a discovery to themselves much longer. After having been told so much, chemists could not be expected to remain quiet under the imputation that they had been eyeless during a whole century, and they would undoubtedly enquire into the matter. Although no one would seek to take the discovery out of the hands of those who had announced it, chemists unquestionably had the right, not only to exercise entire freedom of judgment, but also to critically examine the statements which had been made. With regard to Professor Dewar's observations, which were such as could only be made with the aid of the low temperature appliances at his disposal at the Royal Institution, Professor Dewar would be the first to admit that they were of a qualitative character, and open to several interpretations; but they were certainly highly suggestive.

*75. "*On the Use of the Globe in the Study of Crystallography.*" By J. Y. Buchanan, F.R.S.

The author shows how a globe, on which figures and arcs can be drawn and measured, is serviceable in the study of crystallography exactly as the celestial and terrestrial globes are useful in the study of astronomy and geography. All the problems to which spherical trigonometry is usually applied can be readily solved by graphic constructions on the globe with an exactness which depends on the size of the globe and the refinement which has entered into its construction, and into that of the divided circles with which the measurements are made.

Mr. Bourne, with the aid of lantern slides, described a projective goniometer, independently designed and constructed on the same principle as that advocated by Mr. Buchanan, by Miss Edna Walter, and himself, which was exhibited at the Royal Society's Soirée in June last.

A hollow metal sphere is supported on a horizontal axis, while the crystal to be measured is supported on a second axis parallel to and in the same vertical plane as the former. These two axes pass through the centres of two metallic discs of exactly the same circumference; the discs are geared together by two steel bands, so that they can rotate at the same speed without backlash, the sphere and crystal moving through the same angle. The discs are fixed to a heavy framework which can rotate about an imaginary vertical line, passing through the centre of the sphere and cutting the two supporting axes at right angles. By means of rotation about its two axes the crystal can be turned into any position whatever, and the sphere moves with exactly the same angular velocity. The two motions are controlled by two convenient handles. The usual arrangement of collimator and telescope is fixed in front of the crystal. A movable lens converts the telescope when required into a microscope, and the crystal can be rotated until any particular face is approximately perpendicular to the line bisecting the angle between collimator and microscope. The microscope lens is then removed, and the crystal is finally adjusted till an image of the signal attached with collimator is seen to intersect the lens wires in the telescope. In order that the best part of any face may be in the field of view, an adjustment allows telescope and collimator to move either vertically or horizontally parallel to the face. When the crystal face is thus in position a cross is printed on the sphere at such a spot that the radius of the sphere through the centre of the cross is parallel to a normal of the crystal face. Each face of the crystal is seen brought into the same position, and its pole marked upon the sphere. A complete projection is thus obtained, and the angles between the poles can be measured with a graduated arc. The accuracy with which this can be done depends, of course, upon the diameter of the sphere. In this particular instrument the diameter is 6 in., and it is possible to measure to within about 20 min. The working mechanism consists of a small india-rubber stamp, curved to fit the sphere, and having two fine intersecting raised curves upon it. It rests against a pad soaked with aniline dye and varnish, and moistened with alcohol; the latter rising through a slide from a tube below. On pressing a lever the stamp moves round a vertical axis and presses against the sphere at the right spot.

*76. "*A New Method of obtaining Dihydroxytartaric Acid, and the Use of this Acid as a Reagent for Sodium.*" By H. J. H. Fenton, M.A.

In a former communication a new acid was described, which is obtained by oxidation of tartaric acid in presence of iron. The formula of this acid is $C_4H_4O_6$. It is dibasic, and crystallises with $2H_2O$. The molecule of this crystallised acid contains, therefore, two atoms of hydrogen more than that of dihydroxytartaric acid, and it is now shown that it readily yields the latter acid on oxidation. If bromine be employed as the oxidising agent, the change takes place quantitatively, according to the equation $C_4H_4O_6{\cdot}2H_2O+Br_2=C_4H_6O_8+2HBr$. The solution so obtained gives a white crystalline precipitate of the nearly insoluble sodium salt when neutralised with sodium carbonate. The yield of sodium salt does not fall far short of the theoretical.

From this salt the free acid is easily obtained by Miller's method (*Ber.*, 1889, 2015).

Since free dihydroxytartaric acid can be so readily obtained in this way, the author suggests its use as a reagent for the detection of sodium. The test is fairly delicate, and does not appear to be influenced by the presence of potassium or ammonium salts.

*77. "*Essential Oil of Hops.*" By Alfred C. Chapman.

In a preliminary communication to the Society (*Proc.*, 1893, 177) the author gave a brief account of a sesquiterpene prepared from the essential oil of hops by fractional distillation. Since then three other and much larger samples of the essential oil have been more fully examined with more definite results. All of these samples are of known origin and genuineness. The relative densities and specific rotatory powers having been determined, these samples of oil were submitted to fractional distillation under a pressure of 60 m.m. of mercury, the fractions of corresponding boiling points being mixed after their identity had been ascertained.

After prolonged fractionation the following fractions were obtained, (1) 86—91°; (2) 145—150°; (3) 163—168°; (4) 168—173°.

Nos. 1 and 4 were the main fractions, the remaining two being small. Fraction No. 4 corresponded to nearly two-thirds of the oil used.

These fractions were then submitted to a careful investigation.

Fraction No. 1 was a colourless mobile liquid of characteristic smell. After purification by distillation over sodium under a pressure of 50 m.m. it boiled at 86—89° at atmospheric pressure; b. p. 166—171°, rising afterwards to about 230° owing to polymerisation and oxidation. Its relative density at 20°/20° was 0·799, and it was optically inactive. On combustion it gave numbers closely agreeing with the formula $C_{10}H_{17}$; its vapour density also agreed with this formula. Hydrogen chloride was readily absorbed by this fraction, forming an oil which was, in all probability, a mixture of two distinct hydrochlorides.

Attempts to prepare a nitrosochloride, a nitrosate, and a nitrosite from this fraction failed. It would appear to consist of two hydrocarbons, $C_{10}H_{16}$ and $C_{10}H_{18}$. The latter is probably tetrahydrocymene (b. p. 167°), whilst the former may be one of the "olefinic terpenes" described recently by Semmler. It is at least certain that the greater part, if not the whole, of the lower fraction consists of hydrocarbons other than the ordinary terpenes.

Fraction No. 2 (145—150°) occurred in such small quantities that its complete identification was not possible. It was a colourless oil having a pleasant smell of oil of geranium, with an after-smell of oil of rue. It did not solidify at −10°. Its relative density at 15°/15° was 0·885, and, on analysis, it gave numbers agreeing with those required for the formula $C_{10}H_{18}O$. It united readily with bromine, and in many of its properties appeared to bear some resemblance to geraniol.

Fraction No. 3 (163—168°) was a small fraction which was found to be a mixture of fractions 2 and 4.

Fraction No. 4 (168—173°) was by far the largest. It consisted of a sesquiterpene, $C_{15}H_{24}$; the following are its chief properties. Boiling point, 263—266° (corr.); relative density at 15°/15° = 0·9001; molecular refraction 66·2, a sesquiterpene with two pairs of "doubly-linked" carbon atoms requiring 65·7; it was optically inactive, and unites with 4 atoms of bromine to form an oily bromide. The dihydrochloride could not be crystallised. With nitrosyl chloride it unites, forming a white crystalline nitrosochloride melting at 164—165°. With piperidine this nitrosochloride reacts readily, forming a crystalline nitrol piperide melting at 153°.

This sesquiterpene is not identical with either cubebene (cadinene), caryophyllene, clovene, or cedrene, the only four sesquiterpenes of which we possess any definite knowledge, and it is therefore proposed to name it "humulene." In three out of the four samples of oil examined humulene was the main constituent.

78. "*Interaction of 1 : 2-Diketones with Primary Amines of the General Formula* $R'{\cdot}CH_2{\cdot}NH_2$. *Second Notice.* By Francis R. Japp, F.R.S., and W. B. Davidson, M.A., B.Sc.

In a previous note on the interaction of benzylamine and benzil in presence of zinc chloride (*Proc.*, 1894, 49), the authors showed that these substances yield tertiary and quaternary benzyl-derivatives of lophine. The present communication deals with results obtained in the study of analogous interactions.

Benzil and ethylamine interact according to the equation—

$$\begin{matrix} C_6H_5\cdot CO \\ | \\ C_6H_5\cdot CO \end{matrix} + 2C_2H_5\cdot NH_2 = = \begin{matrix} C_6H_5\cdot C\cdot N(C_2H_5) \\ \| \\ C_6H_5\cdot C \text{———} N \end{matrix}\!\!>\!C\cdot CH_3 + 2H_2O + H_2,$$

yielding *N-ethyl-diphenyl-μ-methyl-imidazole*, which forms lustrous prisms melting at 125·5°. When zinc chloride is present, a chloride of a quaternary base appears to be formed at the same time, as in the benzylamine interaction, but was not isolated in a state of purity. The constitution of the foregoing imidazole was proved by preparing it by the action of ethyl iodide on diphenyl-μ-methyl-imidazole. It also unites with ethyl iodide to form a quaternary iodide—

$$\begin{matrix} C_6H_5\cdot C\cdot N\nu I(C_2H_5)_2 \\ \| \\ C_6H_5\cdot C \text{———} N \end{matrix}\!\!>\!C\cdot CH_3 \text{ (m. p. 163°)}.$$

The action of methylamine on phenanthraquinone has been studied by Zincke and Hof (*Ber.*, xii., 1644), who obtained a base to which they assigned the formula $C_{16}H_{18}N_2$. The present authors find, however, that the formula is $C_{16}H_{12}N_2$. The compound is formed in an interaction strictly analogous to that which occurs with benzyl and ethylamine, and its constitution is doubtless that of *N-methyl-diphenylene-imidazole*—

$$\begin{matrix} C_6H_4\cdot C\cdot N(CH_3) \\ \| \\ C_6H_4\cdot C \text{———} N \end{matrix}\!\!>\!CH.$$

The melting-point was found at 188° (185—186°, Zincke and Hof).

Phenanthraquinone and benzylamine yield *diphenylene-μ-phenyl-oxazole*—

$$\begin{matrix} C_6H_4\cdot CO \\ | \quad | \\ C_6H_4\cdot CO \end{matrix} + C_6H_5\cdot CH_2\cdot NH_2 = = \begin{matrix} C_6H_4\cdot C\cdot O \\ | \quad | \\ C_6H_4\cdot C\cdot N \end{matrix}\!\!>\!C\cdot C_6H_5 + H_2O + H_2,$$

whilst, at the same time, a sparingly soluble compound of high melting-point is formed, which appears to have the formula $C_{28}H_{17}NO$, but is difficult both to purify and to analyse.

79. "*The Isomeric Dinitrodiazoamidobenzenes and their Melting-points.*" By R. Meldola, F.R.S., and F. W. Streatfeild.

The authors have made a careful series of comparisons between their former preparations of diparadinitrodiazoamidobenzene and specimens placed at their disposal by Drs. Pawlewski and Bamberger. They find all three products to be identical, and have come to the conclusion that in this case there is no reason to suspect stereochemical isomerism in the sense advocated by Hantzsch. The discrepancies in the melting-points given by different observers has been found to be due to the circumstance that the compound has no definite melting-point, but a point of decomposition, as they had already stated in former papers. They have found that the pure compound can be made to melt at 220—236°, according to the rate at which the thermometer is raised. The hitherto unknown diortho-compound,—

$$(o)NO_2\cdot C_6H_4\cdot N_3H\cdot C_6H_4\cdot NO_2(o),$$

has been prepared, and consists of golden yellow scales melting without decomposition at 196—196·5°. This compound has all the properties of a true diazoamide; it is acid in character, and forms salts which are somewhat unstable. The "protecting influence" of the nitro-group in the ortho-position renders the formation of alkyl ethers difficult, if not altogether impossible, and the authors have not yet succeeded in alkylating the compound.

80. "*On the Yellow Colouring Matter of 'Sophora japonica.'*" By Edward Schunck, Ph.D., F.R.S.

The undeveloped flower buds of *Sophora japonica*, a leguminous plant growing in the North of China, contain a yellow colouring matter which has been examined several times without any definite conclusion having been arrived at. Foerster, considering it as a peculiar substance, called it *sophorin*, but the author's experiments show that it is identical with rutin, the colouring matter of garden rue and other plants. It yields, on hydrolysis, quercetin and rhamnose. The numbers obtained by analysis corresponded with the formula $C_{27}H_{32}O_{16}$, in accordance with which its decomposition by hydrolysis would be represented by the following equation:—

$$C_{27}H_{32}O_{16} + 3H_2O = C_{15}H_{10}O_7 + 2C_6H_{14}O_6$$

Herzig's formula, $C_{15}H_{10}O_7$, was adopted as representing the composition of quercetin.

Research Fund.

A meeting of the Research Fund Committee will be held in January. Fellows who wish to obtain grants should send in written applications with full particulars to the Secretaries, at Burlington House, not later than Thursday, January 10th.

THE ROYAL SOCIETY.

Anniversary Meeting, November 30th, 1894.

The Lord Kelvin, D.C.L., LL.D., President, in the Chair.

(Concluded from p. 292).

Copley Medal.—*Dr. Edward Frankland, F.R.S.*

The Copley Medal is awarded to Dr. E. Frankland for his eminent services to theoretical and applied chemistry.

At a time when the classification of organic compounds in homologous series was a comparative novelty, when isomerism was still a profound mystery, and the theory of compound radicles introduced by Liebig was still on its trial, Dr. Frankland made his first attempt (in 1848) to isolate the radicle of common alcohol. Though the attempt was in one sense unsuccessful, inasmuch as the free radicle was never obtained, for reasons which we now more fully understand, the research led to important consequences. The discovery of the organo-metallic compounds, and the study of their composition and properties, was followed by a recognition of the fact, first that the capacity for combination possessed by the atoms of the metals was limited (*Phil. Trans.*, 1852), and secondly that variation of "atomicity," as it was then called, usually occurs by an even number of units (*Journ. Chem. Soc.*, 1866), represented by atoms of hydrogen, chlorine, or such compound racicles as methyl, ethyl, and the rest. These discoveries form the basis of the modern doctrine of valency, with all the important consequences that follow, including the idea of the orderly linking of atoms, and hence the theories of structure or constitution now current.

The discovery of zinc ethyl placed in the hands of chemists an important new instrument of research, which Dr. Frankland was himself the first to use in his investigations concerning the synthetical production of acids o the lactic and acrylic series. Further important synthetical work, conducted in concert with Mr. Duppa,

led to a method of ascending the series of acids homologous with acetic acid.

Dr. Frankland's researches in pure chemistry are almost rivalled in interest by his discoveries in physical chemistry, especially in relation to the influence of pressure on the rate of combustion, on the light emitted during combustion, and on the cause of luminosity in hydrocarbon flames.

The important work done by Dr. Frankland in the study of water supply and sewage, and illuminating gas, has proved of great practical value, and has rendered his name famous in connection with the application of chemistry to technical purposes.

RUMFORD MEDAL.—*Prof. Dewar.*

During more than twenty years past Prof. Dewar has been engaged in researches of great difficulty, in the first instance at very high, and latterly at very low temperatures, his inquiries having extended over an extraordinary wide field, as will be seen by reference to the "Royal Society Catalogue" of scientific papers.

In conjunction with Prof. Liveing, he has communicated to the Royal Society a large number of papers which have added much to our knowledge of spectroscopic phenomena.

During recent years he has made the liquefaction of gases a subject of deepest study, and in the course of this work has displayed not only marvellous manipulative skill and fertility of resource, but also great personal courage, such researches being attended with considerable danger. One of his chief objects has been so to improve and develop the methods of liquefying the more permanent gases that it shall become possible to deal with large quantities of liquid, and to use such liquids as instruments of research in extending our knowledge of the general behaviour of substances at very low temperatures. In this he has already been highly successful. Not only has he succeeded in preparing large quantities of liquid oxygen, but he has been able by the device of vacuum-jacketed vessels to store this liquid under atmospheric pressure during long periods, and thus to use it as a cooling agent. Very valuable outcome of these labours has been the series of determinations, made by him in conjunction with Dr. Fleming, of the electrical conductivity of metals at exceedingly low temperatures, which have furnished results of a most unexpected character, and of extraordinary interest and importance. Prof. Dewar's experiment showing the great magnetic susceptibility of liquid oxygen is exceedingly important and interesting. His recent observations on phosphorescence, and on photography (*Chem. Soc. Proc.*, June 28, 1894), and on ozone (*Phil. Mag*, August, 1894, pp. 238, 239) at very low temperatures, have given surprising results of a highly instructive and interesting character. It is difficult to exaggerate the importance of extending these researches, which certainly deserve all possible encouragement and support. The award of the Rumford Medal to Prof. Dewar is made in recognition of the services which he has rendered to science by the work which he has already done and the provision he has been successful in making for future work, in the investigation of properties of matter at lowest temperatures.

ROYAL MEDAL.—*Prof. J. J. Thomson, F.R.S.*

Prof. J. J. Thomson has distinguished himself in both mathematical and experimental fields of work. His first essay on vortex rings showed power of grappling with difficult problems, and added to our knowledge concerning the encounter of rings which came within a moderate distance of one another so as to deflect each others' paths.

His theoretical work in the borderland of chemistry and physics has been very interesting and suggestive. His experimental work has likewise been mainly on the borders of chemistry and physics. He has observed the large conductivity of many gases and vapours, and proved the non-conducting power of several others, founding on the conducting power of iodine vapour important speculations as to its probable chemical constitution.

He has also measured the specific resistance of various electrolytes, under extremely rapid electric oscillations, by an ingenious and valuable method, based on the partial opacity of semi-conducting matter to electromagnetic waves. Recently he has worked at the discharge of electricity through rarefied gases, getting induced currents in closed circuits in sealed bulbs without electrodes, and, in especial, measuring to a first approximation the absolute velocity of the positive discharge through a long vacuum tube, proving that it was comparable with, though decidedly less than, the velocity of light. He also gave an ingenious theory of the striæ—a theory which he has since endeavoured, with some success, to extend to a large number of electrical phenomena, the whole of electric conduction and induction being regarded by him from the chemical side as a modified or incipient electrolysis, or as concerned with electrolytic chains of molecules or "Faraday tubes."

Some of his recent mathematical work on the theory of electric oscillations in spheres and cylinders, and in dumbbell oscillators of the kind used by Hertz, with reference to not only their oscillation-frequency but also their damping efficiency, has been of much service to experimental workers in those branches of physics. And, in general, the effective manner in which he attacks any electrical problem presenting itself, as evidenced by his book on "Recent Researches in Electricity and Magnetism," wherein he worthily carries on into a third volume the great treatise began by Clerk Maxwell, is evidence of consummate ability combined with remarkable energy and power of work.

ROYAL MEDAL.—*Prof. Victor Horsley, F.R.S.*

A Royal Medal is awarded to Prof. Victor Horsley, F.R.S., for his laborious and fruitful researches in physiology and pathology, and particularly for those relating to the functions of the nervous system and of the thyroid gland. His inquiries relating to the former subject have been pursued for more than ten years, and have been communicated to the Royal Society in a succession of papers, the most important of which have been published in the *Philosophical Transactions*. The first of the series of researches (*Phil. Trans.*, 1888), which was conducted in co-operation with Prof. Schäfer, and concerned the relation of a part of the cerebral cortex (the limbic lobe) to sensation, afforded a new confirmation and extension of the doctrine of the localisation of cerebral function now generally accepted. While this work was in progress, Prof Horsley engaged with Dr. Beevor in a long and laborious series of experiments for the purpose of determining with the utmost attainable accuracy the nature of the muscular responses which are evoked by stimulating the convolutions in the quadrumana. The results of these researches were communicated in four papers, of which the first three relate to the "cortical representations" of the movement of the limbs, and of those of the tongue and face (*Phil. Trans.*, 1887-1890); the fourth on the channels (in the internal capsule) by which the cortex exercises its influence on the rest of the nervous system (*Phil. Trans.*, 1890).

These experiments not only served to bring to light a number of new facts, and to elucidate their physiological relations in a very remarkable way, but had a special interest in their bearing on the physiology and pathology of the brain in man. Their importance in this respect is enhanced by the circumstance that in the course of the inquiry the opportunity offered itself of comparing the brain of the monkey with that of the orang (*Phil. Trans.*, 1890), a brain which so closely approaches that of man in its structure that the knowledge acquired by these researches may now be confidently used as a guide in the diagnosis and treatment of cerebral disease. Prof. Horsley has himself shown—and this is not the least of

the merits which it is desired to recognise in the bestowal of the Royal Medal—in how many instances the knowledge which is acquired by patient and skilful work in the laboratory may be made available for the saving of life or the alleviation of human suffering.

In connection with this leading series of researches, two others relating to the physiology of the central nervous system must be referred to. In one of these (*Phil. Trans.*, 1890), Prof. Horsley (in co-operation with Dr. Semon) established the existence, not only of a co ordinating centre in the bulb, but of a cortical area in physiological relation with the respiratory and phonatory movements of the larynx; in the other, in conjunction with Prof. Gotch, he investigated the electrical changes in the spinal cord which are associated with excitation of the cortex and internal capsule, and showed how the observation of these facts can be made available for tracing channels of conduction in the cord.

As regards the thyroid gland, Prof. Horsley's inquiries relating to functions of that organ were like those relating to the nervous system, begun ten years ago, though the results were not communicated to the Royal Society until three years later. Their purpose was to ascertain the nature of the very marked influence which the thyroid was known to exercise on the nutritive functions of the organism, and to show that this influence is constant and definite. In this field, Prof. Horsley has not only the merit of having been one of the earliest workers, but of having at this early period arrived at results which the numerous investigations of subsequent writers have in all essential particulars confirmed.

Davy Medal.—*Prof. Peter Theodor Cleve.*

The Davy Medal is awarded to Peter Theodor Cleve, Professor of Chemistry in the University of Upsala, for his services to chemical science during the last thirty years, and in particular for his long-continued and valuable researches on the chemistry of the rare earths.

This field of inquiry is pre-eminently Scandinavian. By the manner in which he has cultivated it, Prof. Cleve has shown himself a worthy successor of such forerunners as Gadolin, Berzelius, and Mosander, and by sound and patient investigation he has faithfully upheld the traditions inseparably associated with these names. All chemists are agreed that no department of their science demands greater insight or more analytical skill than this particular section. Many of the minerals which furnish the starting-point for investigation are extremely rare, and the amounts of the several earths which they contain are frequently very small. Moreover, the substances themselves are most difficult of isolation, and their characters are so nearly allied that the greatest care and judgment are required in order to determine their individuality.

A remarkable example of Prof. Cleve's power in overcoming these difficulties is seen in his masterly inquiry into the affinities and relations of the element scandium, discovered by Nilson. This, one of the rarest of the metals, is found only in gadolinite to the extent of 0·003 per cent. and in yttrotitanite to the extent of about 0·005 per cent. The whole amount of the material, as oxide, at Cleve's disposal was only about 1 grm., but with this small quantity he determined the atomic weight of the element, and ascertained the characters of its salts with such precision as to leave no doubt of the identity of scandium with the element *Ekabor*, the existence of which was predicted by Mendeléef, in the memorable paper in which he first enunciated the Law of Periodicity. Cleve's research, indeed, constitutes one of the most brilliant proofs of the soundness of the great generalisation which science owes to the Russian chemist.

A not less remarkable instance of Cleve's skill as a worker is seen in his research on samarium and its compounds, which he communicated as one of its Honorary Foreign Fellows to the Chemical Society of London. The existence of samarium was inferred independently by Delafontaine and Lecoq de Boisbaudran, but we owe to Cleve the first comprehensive investigation of its characters and chemical relations. From the nature of its compounds, a large number of which were first prepared and quantitatively analysed by Cleve, and from the value of its atomic weight, which was first definitely established by him, it would appear that samarium most probably fills a gap in the eighth group of Mendeléef's system.

We are further indebted to Cleve for a series of determinations of the atomic weights of the rare substances yttrium, lanthanum, didymium; these are generally accepted as among the best authenticated values for these particular bodies.

No record of Cleve's scientific activity would be complete without some reference to his investigations in the domain of organic chemistry, and more particularly to his studies, extending over twenty years, of naphthalene derivatives. By these researches, made partly independently, and partly in conjunction with his pupils, among whom may be named Atterberg, Widman, Forsling, and Helström, Cleve has gradually brought order out of confusion, and has supplied most valuable experimental evidence of the constitution of naphthalene, and of the course of substitution of naphthalene derivatives. Within recent years a score of workers have occupied themselves with the same field of research, and no greater proof of Cleve's accuracy and care as an investigator could be furnished than the manner in which his naphthalene work—confessedly one of the most intricate and complicated sections of the chemistry of aromatic compounds—has stood the ordeal of revision.

Darwin Medal.—*Right Hon. T. H. Huxley, F.R.S.*

The Darwin Medal is awarded to Thomas Henry Huxley.

Of Mr. Huxley's general labours in biological and geological science I need say nothing here. They are known of all men, and the Society showed its appreciation of their worth when it awarded to him the Copley Medal in 1888. The present medal is a token of the value put by the Society on the part of his scientific activity bearing more directly on the biological ideas with which the name of Charles Darwin will always be associated.

All the world now knows in part, no one perhaps will ever know in full, how, in the working out of his great idea, Darwin was encouraged, helped, and guided by constant communion with three close and faithful friends, Charles Lyell, the younger Joseph Dalton Hooker, and the still younger Thomas Henry Huxley. Each representing more or less different branches of science, each bringing to bear on the problems in hand more or less different mental characters, all three bore share, and were proud to bear share, in aiding the birth of the "Origin of Species." Charles Lyell has long been removed from amongst our midst. Two years ago it was my pleasing duty to place the Darwin Medal in the hands of Joseph Dalton Hooker; that pleasing duty is renewed to-day in now giving it to the last of the three "who kept the bridge."

To the world at large, perhaps, Mr. Huxley's share in moulding the thesis of "Natural Selection" is less well-known than is his bold unwearied exposition and defence of it after it had been made public. And, indeed, a speculative trifler, revelling in problems of the "might have been," would find a congenial theme in the inquiry how soon what we now call "Darwinism" would have met with the acceptance with which it has met, and gained the power which it has gained, had it not been for the brilliant advocacy with which in its early days it was expounded to all classes of men.

That advocacy had one striking mark; while it made or strove to make clear how deep the new view went down and how far it reached, it never shrank from striving to make equally clear the limits beyond which it could

not go. In these latter days there is fear lest the view, once new but now familiar, may, through being stretched farther than it will bear, seem to lose some of its real worth. We may well be glad that the advocates of the "Origin of Species by Natural Selection," who once bore down its foes, is still among us ready, if needs be, to "save it from its friends."

The Society next proceeded to elect the officers and Council for the ensuing year, as follows:—

President—The Lord Kelvin, D.C.L., LL.D.

Treasurer—Sir John Evans, K.C.B., D.C.L., LL.D.

Secretaries—Prof. Michael Foster, M.A., M.D.; The Lord Rayleigh, M.A., D.C.L.

Foreign Secretary—Sir Joseph Lister, Bart., F.R.C.S.

Other Members of the Council—Andrew Ainslie Common, LL.D., William Crookes, F.C.S.; Francis Darwin, M.A.; Andrew Russell Forsyth, Sc.D.; Sir Douglas Galton, K.C.B.; Prof. Alexander Henry Green, M.A.; Sir John Kirk, K.C.B.; Prof. Horace Lamb, M.A.; Prof. Edwin Ray Lankester, M.A.; Prof. Alexander Macalister, M.D.; Prof. John Henry Poynting, D.Sc.; Prof. Arthur William Rücker, M.A.; Osbert Salvin, M.A.; Prof. J. S. Burdon Sanderson, M.D.; Thomas Edward Thorpe, Sc.D; William Henry White, C.B.

CORRESPONDENCE.

THE ACTION OF LIGHT IN SEWAGE TREATMENT.

To the Editor of the Chemical News.

Sir,—Professor Marshall Ward's recent lecture on the "Action of Light on Bacteria and Fungi" (Chem. News, vol. lxx., p. 250) is unquestionably of capital importance to all persons engaged in the treatment of sewage. We too often see precipitation tanks and filter-beds covered over with opaque roofs, so as practically to exclude all light from the water. Surely this mistake, wherever it has been perpetrated, will be speedily rectified.

Again, it has been customary to insist that the clarification of polluted waters is a question of secondary moment. But everyone now, even if he is neither a chemist nor a micro-biologist, must see that suspended matter in any water will powerfully contribute to the exclusion of light from all the water except the merest film on the surface, and hence that clarification, by rendering the free access of light possible, is essential to purification.—I am, &c.,

J. W. Slater.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxix., No. 23, December 3, 1894.

M. Berthelot communicated to the Academy a letter from Prof. R. Fresenius, of Wiesbaden, announcing that the German *savants* have formed at his suggestion a committee of subscription for the monument to Lavoisier. About sixty professors have associated themselves in this work. The Academy is happy at this proof of sympathy for the great French scientist.

Reduction of Alumina by Coke.—Henri Moissan.—This paper will be inserted in full.

Temperature of the Electric Arc.—J. Violle.—M. Moissan has pointed out at one of the recent meetings that the temperature of the arc seems to increase with the intensity of the current. My experiments seem to confirm this view. On taking photographs of the carbons with the required precautions I find that the lustre of the positive crater is the same at 1000 or 1200 ampères or at 10 ampères. This crater is the seat of a physical phenomenon (ebullition of carbon), characterised by a constant temperature. I examined the spectrum of the arc at the same time as that of the positive carbon, and took photographs of both. The distribution of the luminous intensities is different in the two spectra. A large number of rays of the spectrum of the arc are detached brilliantly over the continuous spectrum corresponding to the positive crater. Their lustre varies from moment to moment, and many rays whose prolongations we can scarcely follow across the positive crater are at some moments illuminated for the entire extent of the spectrum. The illumination is the higher as the current is more intense. Kirchoff's laws are here applicable only with a certain reservation. We may doubt if the lustre of the luminous rays constituting the spectrum of a gas is connected with the temperature by the same function as the lustre of the corresponding regions of the spectrum of a solid. This doubt increases when the gas is illuminated under electric action, which seems able to transform itself into light without heat. I estimate that the temperature of the arc is generally higher than that of the positive carbon, and that it increases with the electric energy expended.

Solubility of Ozone.—L'Abbé Mailfert.—The solubility of ozone, for a long time disputed by the most eminent chemists, is now generally admitted. It may be easily verified on collecting concentrated ozone over a water trough; after a certain time the water of the trough exhales a strong odour of ozone. It is the same with water left for a sufficient time in contact with ozone contained in a bottle. This odour is much more manifest when we transfer ozonised water into a flask by means of a syphon. The gas escaping from this water possesses beside the odour all the properties of ozone. It oxidises silver and mercury, forms precipitates of peroxides with the dissolved salts of cobalt and manganese, and forms with ether hydrogen peroxide. These results are also produced with ozonised water, but less easily. Oxygenated water is formed with ether and ozonised water only if the quantity of ozone dissolved is great. In view of these results I ask if we might not utilise the solubility of ozone either to sterilise water under certain conditions or use ozonised water as a disinfectant and antiseptic.

Superposition of the Optical Effects of several Asymmetric Carbons in one and the same Active Molecule.—Ph. A. Guye and M. Gautier.—The authors have previously shown that the two asymmetric carbons of active amyl oxide each act upon polarised light as if all the rest of the mol. were inactive and that their effects were added algebraically. Researches made upon amyl valerianate and amyl glycolate prove that the same rules are applicable when the two asymmetric carbons are different.

Action of the Toxine of Staphylococcus pyogenus upon the Rabbit, and the Secondary Infections which it occasions.—MM. Mosny and G. Marcano.—This paper will be inserted as early as possible.

Action of High Pressures upon some Bacteria.—H. Roger.

Disinfection of Fæcal Matters.—H. Vincent.

MEETINGS FOR THE WEEK.

Thursday, 27th.—Royal Institution, 3. "The Working of an Electric Current," by Prof. J. A. Fleming, F.R.S.

Saturday, 29th.—Royal Institution, 3. "The Working of an Electric Current," by Prof. J. A. Fleming, F.R.S.

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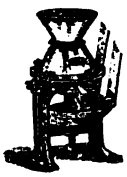

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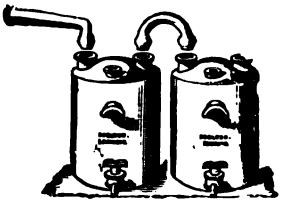

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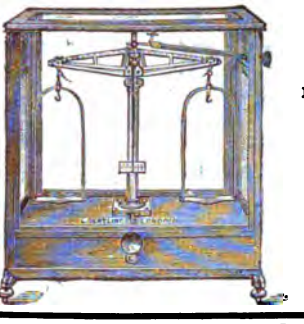

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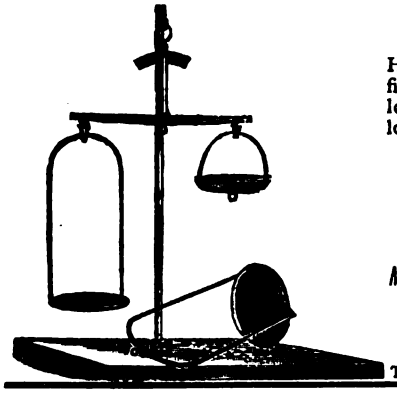

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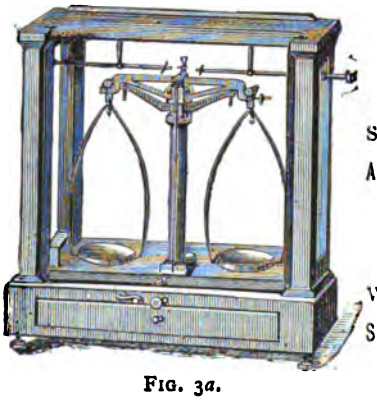

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VOL. LXX., No. 1831.

THE REDUCTION OF ARSENIC ACID BY THE ACTION OF HYDROCHLORIC ACID AND POTASSIUM BROMIDE.*

By F. A. GOOCH and I. K. PHELPS.

IT was shown in a former paper from this laboratory (Gooch and Danner, *Am. Journ. Sci.*, xliv., 380) that arsenic acid may be easily reduced by the simultaneous action of hydrochloric acid and potassium iodide, and more recently (Gooch and Hodge, *Am. Journ. Sci.*, xlvii., 382) this reaction has been successfully applied to the rapid detection of arsenic in presence of antimony and tin, and of antimony and tin associated with arsenic. This paper is the account of work in the course of which it became evident that the action of hydrobromic acid upon arsenic acid is so similar to that of hydriodic acid that potassium bromide may with propriety, and even with advantage, be substituted for the iodide in the process of reduction.

The apparatus which we have used in this work is similar to that employed previously, and is essentially a Mohr's distillation apparatus, consisting of a small flask, of from 25 c.m.³ to 50 c.m.³ capacity, fitted by means of a pure rubber stopper to a pipette which was bent, drawn out at the lower end, and dipped into a test-tube supported and cooled in an Erlenmeyer flask nearly filled with water. The arsenic was introduced into the flask in the form of the pure crystallised dihydrogen potassium arseniate, which was dissolved with 3 grms. of potassium bromide in 5 c.m.³ of water, and 5 c.m.³ of hydrochloric acid of full strength (sp. gr. 1·20) were added. The end of the pipette tube was dipped into 5 c.m.³ of hydrochloric acid of half strength contained in this test-tube used as a receiver, and the distillation was carried on until the liquid in the flask had almost entirely passed to the receiver. The residue was treated with 10 c.m.³ of the strongest hydrochloric acid, and the distillation was repeated with the modification that this time the condensation was effected by passing the volatile material into 10 c.m.³ of water, so that the liquid in the receiver at the end of this operation should have the acidity of hydrochloric acid of half strength. This process of treating the residue with the strongest hydrochloric acid and distilling was continued until arsenic ceased to be discoverable in this distillate. At the beginning of the distillation bromine is liberated and collects in this distillate; but later, as the arsenious chloride volatilises and condenses again, the colour of the bromine in the distillate vanishes with the simultaneous re-conversion of the arsenic to the higher form of oxidation. In such a solution, especially if it is not very hot, hydrogen sulphide precipitates the arsenic only slowly, but the addition of a little stannous chloride dissolved in hydrochloric acid of half strength to the hot solution reduces the arsenic to the lower form of oxidation and prepares the way for the immediate precipitation of arsenious sulphide by hydrogen sulphide. Antimonic acid is likewise reduced under the conditions of the distillation; but, as Koehler has shown (*Zeit. für Anal. Chem.*, xxix., 192), neither small amounts of antimony and tin, which if present originally may pass partially to the distillate, nor the tin added to effect the reduction of the arsenic finally, will be precipitated by hydrogen sulphide under the existing conditions of temperature and acidity.

* Contributions from the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, xlviii., Sept., 1894.

The results of experiment are recorded in the accompanying table.

	Arsenic taken as H_3AsO_4. Grm.	Antimony taken as H_3SbO_4. Grm.	Tin taken as $SnCl_4$. Grm.	Precipitation by H_2S in successive distillates after treatment with $SnCl_2$.	Precipitation by H_2S in the residue dissolved in water.
1.	—	—	—	I. None.	None.
2.	—	—	—	I.—X. None.	Faint colouration.
3.	0·0001	—	—	I. Found. II. None.	None.
4.	0·0010	—	—	I. Found. II. None.	None.
5.	0·0100	—	—	I.—II. Found. III. None.	None.
6.	0·1000	—	—	I.—III. Found. IV. None.	Faint colouration.
7.	0·4000	—	—	I.—VI. Found. VII. None.	Orange precipitation.*
8.	1·0000	—	—	I.—X. Found. XI. None.	Orange precipitation.*
9.	—	0·4000	—	I. None.	Large.
10.	0·0001	0·4000	—	I.—II. Found. III. None.	Large.
11.	0·0001	0·0001	—	I. Found. II. None.	Distinct colour.
12.	0·0010	0·0001	—	I. Found. II. None.	Distinct colour.
13.	0·0100	0·0001	—	I.—II. Found. III. None.	Distinct orange.
14.	—	—	0·4000	I. None.	Large.
15.	0·0001	—	0·4000	I.—II. Found. III. None.	Large.
16.	0·0001	—	0·0001	I. Found. II. None.	Distinct colour.

* Subsequently identified as antimony sulphide by depositing the metal on platinum.

Whenever antimony was introduced intentionally it was taken in the form of antimonic acid produced by oxidising by bromine in alkaline solution tartar emetic purified by boiling with hydrochloric acid until the distillate contained no trace of arsenic. The stannic chloride employed was similarly purified by boiling in strong hydrochloric acid.

It will be seen that no indication was given by hydrogen sulphide either in the distillate or residue when the hydrochloric acid (10 c.m.³) and the potassium bromide (3 grms.) were treated in blank. When the bromide was treated in blank ten times successively no indication was obtained in any individual distillate, but the residue showed a trace of colour which was apparently intensified by the action of hydrogen sulphide. This effect was slight and probably due to the prolonged action of the acid upon the rubber. It is not sufficient to interfere with the detection of 0·0001 grm. of antimony—as subsequent experiments showed.

A single distillation, requiring but three or four minutes, proved to be sufficient for the complete volatilisation of 0·0010 grm. of arsenic, two distillations were enough to remove 0·01 grm., and three 0·1 grm. of arsenic. In handling larger amounts of arsenic, 0·4 grm. or 1 grm. it became evident that the presumably pure arseniate actually contained a trace of antimony, and the efficiency of the bromide treatment in effecting the detection of a little antimony in presence of a large amount of arsenic is clearly shown. It is plain that while the presence of large amounts of antimony and tin tend to diminish the rapidity of volatilisation of the arsenic, the detection of 0·0001 grm. of arsenic is always sure, and that antimony and tin if originally present in appreciable amount will always be discoverable in the residue.

In a comparison of the results of these experiments with those recorded in the former paper describing the reduction by means of potassium iodide, it appears that in general fewer distillations are needed to effect the

transfer of the arsenic to the distillate when the bromide is employed—a condition of affairs which is doubtless due to the fact that in the former treatment an insoluble and somewhat refractory precipitate of arsenious iodide is formed when large amounts of arsenic are present, while the bromide causes no precipitation of the arsenic, and interferes in no way with the distillation of the reduced product.

A COMPARISON OF METHODS FOR THE DETERMINATION OF STARCH.*

By W. E. STONE.

THERE is no longer much doubt among chemists that, in food analysis, the present practice of classifying a large number of widely varying substances under the head of non-nitrogenous extract matter, as a homogeneous material, is wholly erroneous and misleading. The variety of substances covered by this term is well known, and, while it is granted that they are mainly of carbohydrate nature, it is equally clear that, so far as food valuation is concerned, there should be some degree of differentiation between sugars, starches, gums, and the more or less soluble forms of cellulose.

The position of the pentosans in this class of bodies has been pointed out in its different aspects by myself and others at intervals during the past four or five years. It has been shown that these bodies form a distinct constituent of the non-nitrogenous extract matter to a greater or less degree in all fodder articles; that under present analytical methods their individuality as food constituents is wholly merged into that of the more valued carbohydrates; some light has also been thrown upon their digestibility, and analytical methods of a fair degree of accuracy have been devised for their estimation in the presence of other similar bodies.

Mention is made of this instance here to show that really some progress has been made, and that, too, within a short time, in our knowledge of what until recently has been an obscure constituent of the non-nitrogenous extract matter.

The object of this present paper is to call attention along the same line to certain proposed methods for the quantitative estimation of probably the most important of these bodies, viz., starch. At first thought it may appear that the existing methods for the determination of starch are sufficiently satisfactory and accurate; and this is, doubtless, true so far as starch alone is concerned. But it must be remembered that starch almost always occurs in connection with other soluble non-nitrogenous matters, under which conditions its estimation becomes quite another matter and constitutes exactly the question under discussion. The pentosans or gums are, doubtless, the most common of these accompanying substances, and, unfortunately for the analyst, behave toward many analytical methods precisely like starch. Hence, a result which is interpreted to mean starch by a strict adherence to the method may be due, to a very large degree, to other substances. For example, brewers' grains, which from the very process through which they have passed contain little or no starch, will by the ordinary method of inversion and titration be credited with a large amount of starch. Again, hay or straw yield considerable amounts of reducing sugars on inversion, although they contain a minimum of starch, or even none at all. In both these cases the results are due to the inversion of insoluble gums which are present in large quantities.

With these facts in mind it is apparent that a food analysis should give some information with regard to the relative amounts of these different substances present, and should include determinations of the pentosans, sugars, and starches separately.

In this connection the enquiry arises as to how accurately it is possible to determine these bodies as they occur in connection with each other in the ordinary feeding stuffs, by current and accepted methods. As regards the pentosans and sugars, the state of our knowledge seems far more satisfactory than in the case of the starches, in proof of which proposition the following data are offered.

Five methods of starch determination have been compared upon a variety of materials. Four of the methods involve the inversion of the starch and the estimation of the sugar thus formed by volumetric or optical methods; the fourth method is based upon a combination of the starch with one of the alkaline earths. Following are the details of the different methods:—

1. Inversion of the starch with hydrochloric acid and titration with Fehling's solution, known as Sachsse's method. 3 to 5 grms. of the starch-bearing material are heated in a water-bath with 200 c.c. of water and 20 c.c. of concentrated acid, during three hours; the acid is neutralised with soda, the solution filled to 500 c.c., and titrated with Fehling's solution in the usual manner.

2. Inversion with nitric acid and polarisation, proposed by Guichard (*Bull. Soc. Chim.*, [3], vii., 554). Three grms. of the material are heated in a water-bath during one hour with 100 c.c. of 10 per cent nitric acid, filled to 200 c.c., and polarised. The readings are calculated to dextrose.

3. A modification of the preceding. Three grms. of material are heated in the water-bath with 100 c.c. of a saturated solution of oxalic acid during one hour, the object being to bring the starch into solution. The liquid is cooled and filled to 200 c.c. with 10 per cent nitric acid, filtered, and the filtrate heated in the water-bath one hour, attached to an inverted condenser. The solution is then polarised. This method is preferable to the other in that the cellulose and other insoluble substances are removed from the influence of the nitric acid.

4. Inversion of the starch by salicylic acid and polarisation, proposed by A. Baudry (*Zeit. f. Spiritus Industrie*, xv., 41). A normal weight, 5·376 grms., is adopted for the Laurent polariscope. This weight, or some multiple of it, is placed in a 200 c.c. flask with 100 c.c. water and four-tenths to one-half-grm. of salicylic acid, and heated in a water-bath for thirty minutes; fill to within 20 c.c. of the mark with hot water, cool rapidly, clarify by adding a few drops of ammonia, filter, and polarise in a 400 m.m. tube. The readings on the percentage scale indicate percentages. In our practice sodium hydroxide was used instead of ammonia for clarifying.

5. Precipitation of the starch from the condition of paste by barium hydroxide, and determination of the excess of the latter by titration with a standard acid, proposed by A. von Asboth, in 1887. One grm. of the material, from which the fat has been extracted, is boiled with water to convert the starch into a paste; 25 c.c. of a solution of barium hydroxide of known strength is run in, and the whole allowed to cool; then add 100 c.c. of 85 per cent alcohol, and fill to 200 c.c. A compound of starch is formed containing 19·1 per cent of barium oxide, which is precipitated by the dilute alcohol. The solution is filtered, and the excess of barium hydroxide is determined by titrating aliquot portions with standardised hydrochloric acid, using phenolphthalein as an indicator.

The materials to which these methods were applied included nine different samples, as follows:—Pure potato-starch, wheat bran, wheat middlings, wheat flour, dried potatoes, corn-meal, hay, cotton-seed meal, and a mixture of starch, sugar, and dextrine. Four of these were samples sent out by the reporter on feeding stuffs of the Association of Official Agricultural Chemists. Before examination, the samples were extracted with water and ether to remove soluble carbohydrates and fats.

The results obtained are best shown by tabulation, as follows. (See Table).

* Contributions from the Chemical Laboratory of Purdue University. From the *Journal of the American Chemical Society*, xvi., No. 11.

Material.	Inversion by HCl.	Inversion by HNO_3.	Inversion by oxalic acid and HNO_3.	Solution by salicylic acid.	Precipitation by $Ba(OH)_2$.
1. Pure potato starch	85·75	85·50	85·75	85·47	85·58
2. Dried potato	70·92	69·79	68·53	—	64·25
3. Wheat flour	77·69	70·65	65·29	69·38	59·76
4. Corn meal	73·24	66·81	70·55	—	62·11
5. Wheat bran	65·86	40·25	38·68	—	70·77
6. Hay	3·48	19·10	19·10	—	66·47
7. Wheat middlings	30·00	63·09	60·24	—	60·44
8. Cotton-seed meal	4·15	—*	—*	—	54·65
9. Mixture of starch, sugar, and dextrine	9·58	21·00	24·08	18·8	33·99

* These solutions were lævorotatory.

From a survey of these data it appears that any of the methods employed give satisfactory results when dealing with starch alone. It is important to recognise this in order that the responsibility for the discrepancies in connection with the other materials may be properly placed where it belongs, viz., that the variations are due to the complex nature of the materials, and not to the method. Allowing for moisture and cellulose, the starch was pure and each method gave credit for the entire amount present. Turning to the other materials the following is to be noted.

1. Inversion by hydrochloric acid. The starch is converted into dextrose and under carefully controlled conditions the reaction is quantitative. Wohl has shown that a very small quantity of acid is efficient in producing complete inversion (*Ber. d. Chem. Ges.*, xxiii., 2084). According to Märcker, the method of Sachsse here employed gives slightly low results, owing to a slight reduction of dextrose by long heating with the acid. This objection does not appear here in comparison with the other methods. There is undoubtedly danger in the other extreme in not heating long enough. The samples numbered 6, 7, 8, and 9 were treated according to the directions sent out by the A. O. A. C. which call for the removal of heat as soon as the starch-iodine reaction disappears. It is possible that under these conditions. which are accomplished in a very short time, an appreciable amount of starch does not pass beyond the dextrine stage and escapes detection by Fehling's solution. In this connection it is noticeable that the samples 6, 7, 8, and 9 treated in this way, gave lower results by this than by the other methods.

2. The methods calling for the use of nitric acid seem unusually destructive, yet in the case of pure starch they have given results fairly comparable with the others. As originally proposed by the author, it was feared that the cellulose would be attacked, and the use of oxalic acid as in the third method was proposed. This provides for the solution and removal of the starch by a comparatively mild reagent, and this solution is then inverted by the nitric acid apart from the accompanying constituents of the material. The method has a certain advantage of ease and rapidity; the solutions obtained for polarisation are also beautifully clear and admit of accurate readings. The effect of the direct action of the acid in the second method is not so marked as might be expected.

3. Both salicylic and benzoic acids completely dissolve starch; the solutions have a right-handed polarisation and the degree of rotation is directly proportional to the amount of starch present. The method was originally proposed for the valuation of commercial starches, and with such materials is fairly accurate. With feeding stuffs, however, the resulting solutions are frequently too highly coloured and opaque to admit of examination in the polarimeter. The method is therefore of very limited application.

5. The use of barium hydroxide as a means of combining and precipitating starch from solution has attractive features, and has been both highly praised and severely criticised. It necessitates the previous removal of all oils from the material. In our hands the results obtained have been somewhat erratic.

One fact is apparent in connection with the above data, if we leave out of consideration the pure starch sample. The results are more or less discordant and in some cases quite unexplainable. For instance, the hay and cotton-seed meal, when boiled with water, do not give the iodine reaction for starch, yet each of these special methods for the determination of starch credit them with from 4 to 60 per cent of the same. Even fifteen minutes warming with very dilute hydrochloric acid gives an appreciable amount of what we are bound to interpret as starch. This brings us to the inevitable conclusion that other bodies than starch are present and respond toward each of these reactions in the same way as starch does. We know, moreover, that the pentosans are such bodies and that they are invariably present to a greater or less degree in materials of the kind under examination.

In order to obtain some experimental data bearing upon the subject, portions of an isolated sample of pentosans were subjected to each of the methods under discussion. The material was, properly speaking, *xylan*, since on inversion it yields only xylose. It was obtained from wheat straw by boiling the same with lime-water and precipitating the xylan with alcohol. It possessed as high a grade of purity as has thus far been attainable in the preparation of these materials. It was free from any other form of carbohydrate and contained about 6 per cent of ash materials.

One grm. of xylan heated for thirty minutes with 50 c.c. of water and 4 c.c. of strong hydrochloric acid was entirely dissolved. The solution was neutralised and made up to 100 c.c. Of this 6·7 c.c. were required to reduce the copper from 10 c.c. of Fehling's solution, a result equivalent to 67·16 per cent of starch.

One grm. of xylan was heated with 50 c.c. of 10 per cent nitric acid for one hour and became completely dissolved. The solution was made up to 100 c.c. and polarised. The reading was equivalent to that produced by 44·73 per cent of starch.

One grm. of xylan was treated with 50 c.c. of a concentrated solution of oxalic acid for one hour, by which it became completely dissolved, made up to 100 c.c. with 10 per cent nitric acid, and heated another hour. The polariscope readings were the same as in the previous case, equivalent to 44·73 per cent starch.

The salicylic acid method was not applicable.

One grm. of xylan was boiled with 30 c.c. of water, 25 c.c. of barium hydroxide solution was added, and afterwards 35 c.c. of 85 per cent alcohol, and the whole made up to 100 c.c. with water. Upon titration of the excess of barium hydroxide, an equivalent of 47·48 per cent of starch was indicated.

These results show conclusively that the pentosan which is most characteristic of feeding stuffs, and which has been shown to occur in all such materials, behaves, towards the reagents named, in precisely the same manner as starch and in a no less marked degree. The conclusion is unavoidable that none of the methods for determining starch, based upon the above principles, can be employed with any degree of accuracy upon grains or forage plants or any materials where the presence of these pentosans is probable.

The most hopeful way of avoiding these difficulties

would seem to be some method of bringing the starch into solution and removing it from its accompanying carbohydrates without any corresponding influence upon them. One method seems to offer this advantage, viz., the application of diastase or malt infusion to the starch containing material. This method is recommended for use among the European experiment stations; it has been shown to yield accurate results with pure starch, and can be objected to, if at all, only on account of length of time required and the difficulty of always having a proper preparation of diastase or malt infusion at hand. These are, however, minor objections in the light of greater accuracy secured. The general features of the method are as follows:—The weighed material is boiled with water (most effectively under pressure) to convert the starch into a paste; after cooling to 65° C. a small quantity of malt infusion is added, and the temperature maintained at 60° to 65° for a half hour. The starch reaction having disappeared the solution may be filtered off, washing the residue thoroughly, the filtrate warmed with a few c.c. of acid to complete the conversion into dextrose, and finally neutralised, made up to definite volume, and titrated. It remains to be seen what the effect of this process may be upon the pentosans or other similar bodies, concerning which there are few data at hand. I have made some preliminary tests which indicate that these bodies are not affected by diastase. One grm. of the xylan, already mentioned, after boiling with water, received 10 c.c. of a fairly strong infusion of malt, and was kept at 65° C. for a half hour. At the same time a sample of starch was boiled to a paste, and treated with the malt infusion in the same way. The starch reaction disappeared and the solution reduced Fehling's solution strongly, but the xylan did not change the Fehling's solution in the least, nor did it appear to have been altered.

It seems, therefore, that in this last method the difficulties presented by the more common methods are to be avoided. The ordinary inversion methods, on the other hand, furnish no accurate conclusion when applied to the determination of starch contained in vegetable tissues.

For assistance in much of the analytical work cited I am indebted to Mr. D. B. Hoffmann.

ON SOLUTIONS OF METALLIC SILVER.

By M. CAREY LEA

The solutions of metallic silver which I have described in previous numbers of the *American Journal of Science* are all colloidal. Since publishing those papers I have examined all the varieties, with the result that none of them will pass through membranes. One of these forms of silver solution, that obtained by the action of ferrous citrate, has also been examined by Mr. Prange and by Dr. Barus with the same result.

The silver solutions are colloidal. But as to whether they are polymerised seems doubtful. Polymerised substances have this property in common, that they are more indifferent than the same substances in their ordinary molecular condition. Now all the varieties of allotropic silver, including the soluble form, are more easily oxidised and chlorised than is silver in its ordinary form. This does not look like polymerisation.

These colloidal solutions of silver are at the least as perfect as those of any other perfectly soluble colloidal substance. A good way of testing for perfect solubility is to observe the liquid under a skylight, letting the incident light make a right angle with the line of view. Many substances which viewed by transmitted light are not only transparent, but brilliantly clear, when examined in the manner just mentioned show unmistakable turbidity.

The solutions of silver stand this test perfectly. This experiment seems to disprove the conclusion arrived at by Drs. Barus and Schneider that this form of silver is not allotropic, but ordinary silver in a state of very fine division (*Zeitschrift fur Physikalische Chemie*, viii., 298). When carefully made they are also very permanent. I have some silver solution made by the action of alkaline hydroxide and dextrine which, after three years' standing, is still strongly coloured. A considerable part of the silver has separated, but as this separation has taken place in the form of bright white metallic silver and has occurred where the light was strongest (the bottle having stood on a table in a well-lighted room), the change seems to have been due principally, if not wholly, to the action of light.

This solution thus maintained so long seemed to afford an opportunity for the rigorous determination of its colloidal nature. Placed in a dialyser at the end of two weeks not a trace had passed through.

These results seem to lead to the conclusion that the silver solutions are colloidal, and yet of a very perfect character, inasmuch as they will bear the same tests for absolute transparency as solutions of crystalloids.—*Amer. Journal of Science*, xlviii., No. 286, October, 1894.

THE QUALITATIVE SEPARATION OF CHROMIUM FROM IRON AND ALUMINIUM.

By R. B. RIGGS.

The separation of chromium from iron and aluminium depends on the conversion of chromium compounds, by oxidation, into soluble chromates. This oxidation is generally effected, either by fusing the hydroxide or basic acetate precipitates with sodium carbonate and potassium nitrate, or by dissolving them in concentrated nitric acid to which potassium chlorate has been added. In the hands of the general student the latter is probably the more satisfactory of the two methods. It is somewhat complicated, however, involving, as it does, the separation of the aluminium by means of potassium hydroxide, solution of the residue in a potassium chlorate-nitric acid solution, and a re-precipitation of the iron.

In many cases the efficiency of hydrogen peroxide, in alkaline solutions, as an oxidising agent, is well known. Its use in converting chromium hydroxide into the chromate was a natural suggestion. A few experiments showed that, under favouring conditions, this change is easily and completely brought about. Solutions containing the equivalent of 0·05 grm. of chromium as hydroxide, 0·3 grm. of sodium hydroxide, and quantities of hydrogen peroxide (15 per cent) varying from 5 to 20 c.c., varying in volume from 50 to 500 c.c., were digested until oxidation seemed* complete. This

* In a majority of the experiments, in the more concentrated solutions, the precipitates disappeared quickly and completely. Where it was necessary to continue the heating for more than ten minutes, there remained an unoxidisable residual which increased rather than diminished on further heating. In all cases prolonged digestion resulted in a precipitation of what proved to be silica. The amount of this precipitate was found to be proportionate to the quantity of peroxide added, and the following experiments showed that it came from the corrosive action of an alkaline solution of the peroxide on the glass. 50 c.c. of water, containing 1 grm. of sodium hydroxide, digested for an hour in glass, remained clear to the end. 50 c.c. of hydrogen peroxide, similarly heated, remained clear, evaporating quietly. 50 c.c. of the peroxide, containing 0·5 grm. of sodium hydroxide, was also similarly digested (the alkaline solution effervesces energetically on being heated). In fifteen minutes the solution had become perceptibly clouded. At the end of an hour, the effervescence having ceased, a considerable precipitate had formed. From 200 c.c. of the peroxide, containing 2 grm. of sodium hydroxide, 4 m.grm. of silica (carrying a trace of iron) were obtained. 500 c.c. of the peroxide, containing 5 grm. of sodium hydroxide, heated in platinum for an hour, remained perfectly clear.

The reagents used were Rosengarten's 15 per cent hydrogen peroxide, 500 c.c. of which gave, on evaporation, a residue of 0·2908 grm. (silica 0·1067 grm., alumina 0·02 grm.), and sodium hydroxide made from sodium.

required from five to fifteen minutes: the more dilute the solution the longer the operation. 5 c.c. of the peroxide was sufficient for the oxidation.

The availability of hydrogen peroxide, as an oxidising agent, having been determined, the influence of its presence on the iron and the effect of dilution on the solubility of aluminium hydroxide in sodium hydroxide solutions, remained to be ascertained. Filtrates from ferric hydroxide, which had been digested in sodium hydroxide solutions containing hydrogen peroxide, gave no sign of the presence of iron except to the sulphocyanide test, showing the influence to be rather favourable than otherwise.

In determining the effect of dilution on the solubility of alumina, quantities of the hydroxide, equivalent to 0·05 grm. of the element, were severally treated with 0·5 grm. of sodium hydroxide in solutions varying in volume from 50 to 500 c.c. In every case solution was effected within five minutes. The influence of dilution was, however, appreciable.

Experiments made to test the practical workings of the method, on mixtures of the three substances, confirmed the observations made in connection with their separate treatments, except that the presence of large quantities of iron hinders somewhat both the oxidation of the chromium and the solution of the aluminium. As to the limits of the method, the impurities, of even the best of available reagents, render the detection of very small amounts of either iron or alumina uncertain. In mixtures containing the equivalents of 0·2 m.grm. each of iron and chromium, and 0·5 m.grm. of aluminium, separations were made, and the several constituents were identified beyond a doubt. With half the above quantities the results were not so satisfactory. The colour tests for both iron and chromium are sufficiently delicate to detect even smaller amounts. The sulphocyanide test will, under favourable conditions (a solution containing not over 1·10 per cent. of hydrochloric acid and an excess of sulphocyanide [5 c.c. 1 : 15]), show the presence of 0·01 m.grm. of iron in 100 c.c. of water (depth of liquid in cylinder 14 c.m.). The yellow colour of sodium chromate is unmistakable in 100 c.c. of solution containing the equivalent of 0·2 m.grm. of the element.

Summary.—The following is an outline of the method of treatment. Given a mixture of the hydroxide or basic acetate precipitates equivalent to 0·1 grm. of each of the three elements. Digest this precipitate in 100 c.c.* of water, to which 10 c.c. of hydrogen peroxide and 1 grm. of sodium (or potassium) hydroxide have been added, until effervescence ceases.† Separate the iron by filtration. Acidify the filtrate slightly with acetic acid and precipitate the alumina by means of ammonia. (Where small quantities are present long-continued boiling and a concentration of the solution may be necessary.) Filter off the alumina and test the filtrate for chromium. The yellow colour of either the iron or alumina filtrates is characteristic. A confirmatory and more delicate test may be made by acidifying the filtrate from alumina slightly and adding a few c.c. of hydrogen peroxide, obtaining the blue colour so characteristic of chromium compounds thus treated.

Note.—Since writing this note my attention has been called to an article by Clark (*Journ. Chem. Soc.*, 1893, i., 1079), on "The Use of Sodium Peroxide as an Analytical Agent." He makes very successful use of this reagent in decomposing ferro-chromium ores, and says that it may be used for the qualitative separation of chromium from iron and manganese, in alkaline solutions, when it acts quickly even in the cold. As compared with hydrogen peroxide, sodium peroxide is the more powerful oxidant, and if the former has any advantage, it is to be found in convenience and, possibly, economy.—*American Journal of Science*, November, 1894.

* The volume will not materially influence the results. Unnecessary dilution is, however, to be avoided.

† If the peroxide be not decomposed there is danger, on acidifying the filtrate containing chromium and alumina, of a reduction of the chromate and consequent precipitation.

OBSERVATIONS ON AMERICAN OIL OF TURPENTINE.

By J. H. LONG.

In the February, 1893, number of the *Journal of Analytical and Applied Chemistry* I called attention to certain peculiarities of our American turpentine oil as distilled from the crude turpentine produced in the southern states.

It is well known that the chief difference between the so-called French and American turpentines is found in their behaviour toward polarised light, the French oil being lævo-rotatory, while that produced here has always been described as dextro-rotatory.

In the course of the examination of a large number of samples distilled in the laboratory from fresh crude turpentine sent me directly, I found that some disclosed a very low rotation, and a few were even lævo-rotatory. Through the courtesy of Mr. E. B. Martin, of Louisville, I was supplied with crude "gum" collected in small amounts from single trees, and from the tests of these samples it appeared that the lævo-rotation was found only in the product from the so-called spruce trees, sparingly represented in the lower turpentine-producing region. As this spruce pine (*P. glabra*) is not considered important from the standpoint of the industry, I found difficulty in securing material enough for satisfactory investigation. However, in April of this year six samples of the dip, or crude liquid exudation, collected near Mobile, from as many different trees, were sent me, and from these I distilled the oils used in the tests below.

In odour, colour, specific gravity, and boiling-point, these oils showed no unusual features, the average specific gravity at 20/4° being 0·862. When examined by the polarimeter, using the 200 m.m. tube, I found the "observed angle of rotation," α, as follows:—

No. 1	α_D = ...	−64·750°
,, 2	,, ...	−69·075°
,, 3	,, ...	−64·541°
,, 4	,, ...	−63·100°
,, 5	,, ...	−63·333°
,, 6	,, ...	−70·333°

The lævo-rotation is in all cases very marked, the specific rotation in the last amounting to—

$$[\alpha]_D = \ldots\ldots\ldots\ldots -40{\cdot}79°.$$

It is also interesting to note that the results are close for the six samples, but as the trees yielding them grew in the same orchard, and, therefore, under practically the same conditions, and as the samples were taken at nearly the same time, this agreement should not be unexpected. It may be recalled that the lævo-rotation of the French oil has usually been found much more uniform than the rotation of the American oil.

These observations seem to show the probable correctness of my former suggestion, viz., that the negative rotation sometimes found in American oil may be due to the presence of products from spruce trees. This appears all the more probable when it is remembered that in numerous oils examined, known to be free from spruce, a marked positive rotation was always noted, while a low positive rotation was found only in those oils distilled in parts of the country where the spruce is occasionally found.

In the further study of these oils I mixed distillates 1 and 3 above and re-distilled fractionally. The fractions were polarised as before, with the following results:—

Temperature.	a_D in 200 m.m. tube.
156·0 to 156·7	−69·133°
156·7 ,, 157·2	−67·683°
157·2 ,, 157·6	−65·930°
157·6 ,, 159·4	−63·200°
159·4 ,, 162·7	−57·883°

A mixture of 2 and 6 gave:—

Temperature.	a_D in 200 m.m. tube.
156·0 to 156·2	−73·350°
156·2 ,, 156·7	−72·416°
156·7 ,, 157·2	−71·066°
157·2 ,, 158·7	−68·865°
158·7 ,, 162·7	−65·160°

These results confirm those obtained from other oils showing that the absolute amount of rotation is decreased in the higher fractions.

It was stated by Berthelot (*J. B.*, 1853, p. 522) that the dextro-rotatory American oil, when heated in sealed tubes to above 250°, is transformed into a substance with higher boiling-point and negative rotation. To test this behaviour in the present case I heated a portion of the first fraction from 1 and 2 to a temperature of 280° during two hours in a sealed glass tube. On cooling, it was polarised without re-distillation, and showed in the 200 m.m. tube—

$$a_D = \ldots\ldots\ldots\ldots -15{\cdot}33°.$$

The product was then sealed and heated again to 300° through several hours. On cooling, it was found to be yellowish and somewhat viscid; on distillation the liquid was found to have a much higher boiling-point than the original turpentine, but little passing over below 170°.

Three-fourths of the product distilled between this point and 250°, and this portion polarised, gave in the same tube—

$$a_D = \ldots\ldots\ldots\ldots -19{\cdot}560°.$$

A fraction of the distilled liquid collected from 175—180° was strongly lævo-rotatory also.

The residue was very dark and became thick and resinous on exposure to air. The distilled liquid had a marked odour of oil of lemons, and this with its rotation suggest that it must be identical with the product described by Berthelot as iso-terebenthene, which may be obtained also from the lævo-rotatory French oil. While the ordinary product of long heating of turpentine oil seems to be inactive dipentene, we have here a very stable active product which is probably mainly lævo-limonene.—*Journal of the American Chemical Society*, xvi., No. 12, December, 1894.

THE ACTION OF HIGH PRESSURE UPON SOME BACTERIA.

By H. ROGER.

Several experimentalists have examined the action of compressed gases upon bacteria and by using oxygen or carbonic acid at relatively low pressures have succeeded in attenuating or even destroying them. The question which I have taken up is different. I have studied the action exerted upon these organisms by the compression of the liquids in which they vegetate.

A first series of experiments was executed by means of a very ingenious apparatus devised by M. Gozand. It consists essentially of a cistern of cast-iron filled with water; its upper extremity has an aperture in which there slides with gentle friction a copper cylinder which closes it hermetically; a heavy mass of metal can fall upon this cylinder from a height of 3 or 4 metres, when the shock produced is equal to an increase of pressure of 200 to 250 kilos. per square c.m.

The cultures used in our researches had been made in broth. We introduced 1 c.c. into small caoutchouc sterilised tubes closed at each end, and they were immersed in the liquid of the apparatus and underwent from five to ten successive shocks. The microbes employed, *Staphylococcus aureus*, *Bacillus coli*, the *Streptococcus* of erysipelas, and the microbe of splenic fever, whether with or without spores, were not at all affected by these mechanical actions; their vegetative character, their form, their functions and their virulence underwent no appreciable modification.

In view of these negative results, I undertook another series of experiments, which were performed at the works of M. Bourdon, by means of the apparatus which serves for graduating manometers. The cultures were submitted to pressures of 1000, 2000, and 3000 kilos. per square c.m. The duration of the experiment was six minutes for pressures of 1000 kilos., twelve minutes for those of 3000 kilos. It required ten minutes to reach this high pressure, which was then kept up for two minutes; the release was effected in from five to ten seconds. This last detail has a great importance, for it is perhaps to this rapid release that some of the results obtained must be attributed.

Under these conditions the *Staphylococcus aureus* and the *Bacillus coli* experienced no injury, the former especially retaining its chromogenous power.

The *Streptococcus* supported perfectly 1000 kilos., but a pressure of 3000 kilos. modified the cultures; the microbia were killed to the extent of one-third, those which resisted developed more slowly than the check specimens, and presented a less virulence. Rabbits inoculated under the skin of the ear with normal cultures succumbed in five or six days to a generalised infection without any local lesion; those which received compressed cultures were attacked with an erysipelas from which they recovered in nine or ten days.

The effects produced by the microbe of splenic fever varied notably according as it was sporiferous or non-sporiferous. The sporulated microbe after it had supported a pressure of 3000 kilos. grows as well as previously, but its virulence is slightly diminished; guinea-pigs inoculated with it perished two or three days later than the check-subjects.

If the cultures are non-sporogenous the results are much more distinct. Up to 1000 kilos. we observe no modification; but at 2000 and 3000 kilos. a great number of the rods were killed. Before compression the cultures on plates produced numberless colonies. After having been exposed to pressures of 2000 to 3000 cultures, the culture liquids, if studied in the same manner, gave nearly 50 to 60 colonies in the former case, and from 16 to 19 in the latter. The virulence of the microbia which had resisted was diminished in notable proportions; instead of killing the guinea-pigs in three or four days, the cultures which had been exposed to 2000 kilos. proved fatal only in twelve or thirteen days, and those which had been subjected to 3000 kilos. did not occasion death before eighteen or nineteen days. We thus create a chronic malady analogous to that which Physalix has obtained on inoculating certain vaccines for splenic fever.

There exists, therefore, a great difference between the sensitiveness of bacteria to the action of compressed gases and their resistance to simple elevation of pressure. They must be exposed at least to 2000 or 3000 kilos. to occasion in some species appreciable injury.

It may still be asked whether in the latter case the effects are not due to the thermic rise produced by compression. Captain Meillet has calculated that if all the work produced was transformed into heat the increase of temperature would not amount to 5·3° for 3000 kilos. The effects produced must therefore be ascribed to the increase of pressure.—*Comptes Rendus*, cxix., No 23, December 3, 1894.

ON THE

ACTION OF THE TOXINE OF STAPHYLOCOCCUS PYOGENUS UPON THE RABBITS AND ON THE SECONDARY INFECTIONS WHICH IT DETERMINES.

MM. MOSNEY and G. MARCANO.

Intraveinous inoculation of large doses of filtered cultures of *Staphylococcus pyogenus aureus* occasioned the death of rabbits in a few seconds, but the animals survived doses of 1 to 2 c.c. They are by no means vaccinated against the action of living and virulent cultures of the above *Staphylococcus*. On the contrary a previous injection of filtered cultures seems to favour the pathogenous action of this microbe.

The surviving animals quickly recovered, but after about four to five weeks they became emaciated, a profuse diarrhœa set in without apparent cause; the temperature fell to 37° or 36°, and death occurred in two or five days.

The autopsy always revealed the same lesions, which never extended beyond the limits of the abdominal cavity.

Bacteriological examinations, colourations, and cultures always showed the presence of microbia, which, according to ulterior researches on the normal contents of the intestine of rabbits, are the habitual inmates of this cavity.

The inoculation of these microbia, whether taken from the intestine or from the presence of rabbits which had perished, remained without results if effected in the peritoneum. But an intraveinous inoculation killed the animal in less than twenty-four hours by septicæmia and without any apparent lesion.

The totality of these experiments proves that the introduction of a toxine into the economy may, without occasioning any immediate catastrophe, set up the escape from the intestine of microbia which are there met with in a normal condition, and that these microbia, inoffensive in the bowel, become pathogenous when they escape from it under the influence of a septic affection, and determine in their new medium severe suppurations which sooner or later involve the death of the animals.

Human pathology offers numerous instances of these morbid predispositions created by interior infections which effect a transformation of micro-organisms simply saprophytic in appearance, and the habitual and harmless inmates of the healthy organism into pathogenic microbia.—*Comptes Rendus*, cxix., 962.

ON LUMINOUS PHENOMENA DURING CRYSTALLISATION.

By Dr. ERNST BANDROWSKI.

Single observations of the luminosity of certain substances during crystallisation have been made long ago. Thus it is universally known that arsenious anhydride in its amorphous state gives out light when crystallising from a hydrochloric solution.

A similar phenomenon occurs during the crystallisation of the double salt of potassium and sodium sulphate fused previous to solution. Berzelius and Rose state that a saturated solution of sodium fluoride on very slow evaporation gives off many pale yellow sparks.

The cause of this interesting phenomenon is as yet perfectly unknown. It is generally connected with the act of cystallisation itself in the belief that the luminous phenomena are a consequence of the collision of single mols. during the formation of crystalline complexes. This certainly plausible view has hitherto not been experimentally tested from want of systematic observations on a sufficiently large series of substances, and the phenomenon itself has to some extent fallen into oblivion despite its interesting character.

On the basis of the doctrines of electrolytic dissociation, I proposed to myself the question whether the luminous phenomena during crystallisation may not be the consequence of electric discharges? If the mols. of many substances in solutions—especially aqueous—are dissociated into those particles which are separated out under the influence of electric currents, the hypothetical inference seemed to me justified that the separation of different bodies from their solutions may be a complicated process and ensues in two phases; in the former the originally free ions unite to molecules, which in the later phase coalesce to crystalline complexes. The first act of this process, the union of the electrically antagonistic ions, might be the cause of the luminous phenomena.

This hypothesis admits of certain conclusions which may be experimentally tested, and which led me to undertake researches on the luminosity of crystallising bodies.

I here venture to make known the first results of these investigations, in the hope of being able to furnish further contributions to the solution of the question.

The first conclusion of my hypothesis was this: that the luminous phenomena of crystallisation are universally perceptible in those cases in which there occurs an electrolytic dissociation. In consequence I took up the examination of some simple salts which undergo electrolytic dissociation, but concerning the luminosity of which nothing is known. The results are as follows:—The development of light is observed on the crystallisation of sodium chloride, potassium chloride, bromide, sulphate, and nitrate from aqueous solutions. Successful results were observed on precipitating such salts from their aqueous solutions by additions of hydrochloric acid or alcohol. Sodium chloride gave a striking result on treatment with hydrochloric acid. The light is of a greenish blue colour and of considerable intensity. With alcohol the effect is slighter, but more permanent. With potassium chloride the effect is nearly equal to that with sodium chloride, but stronger if alcohol is used as a precipitant.

Very numerous experiments are necessary and prolonged practice.—*Zeitschrift für Physikalische Chemie*, xv., Part 2, p. 321.

NOTE ON THE TEST FOR STRYCHNINE.

By W. P. MASON and J. W. BOWMAN.

Organic matter having been removed, and the solution containing the purified alkaloid having been evaporated to dryness on the water-bath, the dry residue is taken up with a little concentrated sulphuric acid, one of several oxidising agents added in solid form, and the well-known strychnine colour reaction forthwith appears as usual. Or, in the event of the evaporation having been accomplished in a platinum dish, such dish may be connected with the positive pole of a battery, and, upon touching the negative pole to the acid contents, the strychnine colour instantly flashes out. All this being long since known, the following table is offered to indicate the relative degrees of delicacy of the several reagents commonly employed.

In each instance the figures at the top indicate the number of m.grms. of strychnine sulphate actually operated upon, *i. e.*, the amount left upon the evaporating dish by the evaporation of the measured quantity of standard solution employed.

From the following table it will be seen that beautiful as Letheby's galvanic test is, it does not compare favourably in point of delicacy with the more common ones using chemical reagents. It certainly fails long before the bitter taste disappears.

Amount used in m.grms.	0·500.	0·400.	0·300.	0·250.	0·150.
$K_2Mn_2O_8$	Very strong.	Very strong.	Very strong.	Very strong.	Strong.
$K_2Cr_2O_7$	Very strong.	Very strong.	Very strong.	Very strong,	Strong.
PbO_2	Fair.	Fair.	Weak.	No test.	No test.
$K_6Fe_2(CN)_{12}$..	Strong.	Strong.	Strong.	Strong.	Strong.
MnO_2	Strong.	Strong.	Strong.	Strong.	Strong.
H_2CrO_4	Very strong.	Very strong.	Very strong.	Strong.	Strong.
Battery	Strong.	Fair.	No test.	No test.	No test.

Amount used in m.grms.	0·050.	0·025.	0·020.	0·015.	0·010.
$K_2Mn_2O_8$	Strong.	Strong.	Weak.	Very weak.	No test.
$K_2Cr_2O_7$	Fair.	Weak.	Very weak.	No test.	No test.
PbO_2	No test.	No test.	No test.	No test.	No test.
$K_6Fe_2(CN)_{12}$..	Fair.	Fair.	Weak.	Very weak.	No test.
MnO_2	S rong.	Fair.	Weak.	Weak.	Very weak.
H_2CrO_4	Weak.	No test.	No test.	No test.	No test.
Battery	No test.	No test.	No test.	No test.	No test.

From the table it would seem that MnO_2 should be given the first rank, but the slowness of its action is greatly in its disfavour, and the consequent difficulty of getting the colour to flow down the side of the dish from the crystal of reagent is an objection. The presence of a little organic matter also masks its action.

Altogether, we found that $K_2Mn_2O_8$ gave the most satisfactory results. Of course, the colour of this reagent is an argument against its use, but if the acid used be of full concentration, and if a blank experiment be run at the same time with acid only in the dish, no trouble need be feared from that source.—*Journal of the American Chemical Society*, xvi., No. 12.

THE FOUNDATIONS OF A NEW SYSTEM OF THE ELEMENTS.

By J. TRAUBE.

THE properties of the elements are periodic functions of their atomic weights.

This proposition is placed at the head of those systems of the elements which during the last decennia have found the most general recognition. Still, certain defects of the system have not been overlooked from any side, and all the attempts to cover these defects have led to new shortcomings.

In various cases an element does not occupy that place in the system which is due to it on account of its relations of affinity. In many cases an element resembles several elements in different groups, but in the system there can be assigned to it only one place. Lastly, the hypothesis of the unity of matter, which is now very probable, speaks against the assumption that among the properties of the elements the atomic weight alone should be regarded as decisive.

Hence a too one-sided principle seems to lie at the foundation of the system.

A constant, no less fundamental than the *mass* of the atom, is the *space* which the atom occupies.

For the atomic volumes there appear—as a foregoing memoir shows—at least as simple relations as for the atomic weights.

I hold the attempt as justifiable to place at the head of a new system of the elements the proposition, "The properties of the elements are in the first place functions of the atomic weight and the atomic volume."

We would return to the division into a series of natural families.

As an element, according to its valence, obtains a place in different families in the appropriate class of combination, it might be useful to add the short designation mono, di, tri, tetra, as a preliminary syllable for an expression of its valence, *e.g.*, mono-copper, *m*-Cu; di-mercury, *d*-Hg, &c.

The first natural family would include the following elements:—H, Li, Na, *m*-Cu, Ag, *m*-Au, *m*-Hg.

Simple relations of atomic weight can scarcely exist here, the connecting-link being the equality of the atomic volume of all the elements.

A lateral branch of this family includes ammonium and the elements Na—K—Rb—Cs.

The relations of the atomic weights are known; the atomic volumes of the four elements differ by about 10 units; the volume of ammonium is equal to the atomic volume of rubidium. *m*-Thallium stands for the present near potassium.

Much more natural families are in the series of the metals Pb, Ca, Sm, Ba and Mg, Zn, Cd.

Lead, calcium, and strontium, and also magnesium and zinc, have equal or approximately equal atomic volumes; as also barium and cadmium. But for Ca, Sr—Ba, as also for Mg, Zn—Cd, there are for the present only simple relations of the atomic weights established; di-iron has the same atomic volume as *di*-manganese; *di*-copper apparently the same as *di*-nickel. A more precise classification is, as well as in other di- and tri-valent metals, not yet possible.

The two groups, each of three platinum elements, are apparently linked together by the equality of the atomic volumes. At least this may hold good for Pt and Pd, as also for Ir. Molybdenum and tungsten have equal atomic volumes.

Among the non-metals, we found for Fl—Cl, O—S, N—P equal differences of atomic weights and atomic volumes.

The elements *m*-Cl—*m*-Ba—*m*-I, S—Se—T, P—As—Sb, N—Ti—Zr form, as regards the volumes, arithmetical series with apparently equal or nearly equal differences.

Chlorine is connected with bromine in the chlorates and bromates, with manganese in the perchlorates and permanganates by equality of volume in corresponding compounds; as also nitrogen with vanadium, carbon with silicon.

These indications may suffice. We have to treat here merely of a meagre skeleton of this new system. Further and numerous researches are needed in particular with atomic solutions of the elements, as such must be brought into consideration by examinations of alloys, &c.

Already we may see, as it appears to me, certain advantages of the new arrangement.

The inequalities of the periodic system will be removed.

Even when in closely connected elements (*e.g.*, Co and Ni) there appear no simple relations of the atomic weights, the link is established by the relations of the atomic volumes.

The possibility of variation in space on the part of the atoms, or polysterism, is the most intimate casual connection with the fact that an atom may change its properties in accordance with its valence, and must obtain its place in different families accordingly. *m*-Copper belongs

to silver, and *di*-copper to zinc and nickel.—*Berichte*, 1894, No. 18.

REMARKS ON COLLOIDAL SILVER.

By C. BARUS.

1. In the absence of Dr. E. A. Schneider I wish to say that there does not seem to be any real issue between the recent note of Mr. Carey Lea (*American Journal of Science*, October, 1894) and our own work (Barus u. Schneider, *Ostwald's Zeitschrift*, viii., p. 278, 1891; *Wied. Annalen*, xlviii., p. 327, 1893; full references to the above and other allied physical questions are there given). It was our endeavour to arrive at new data relative to colloids in general, and colloidal silver was chosen merely as a promising subject for attack. We showed at length that colloidal silver possesses properties which can be explained with reference to the analogous behaviour of suspended sediments. Differences necessarily remained as a result of differences in the size of particles in the two cases, the silver being much more finely comminuted. For this reason we cannot admit that Mr. Lea's recent experiment is decisive. A similar test had already been made by Prange (*Rec. des Trav. Chim. des Pays-Bas*, ix., p. 125), and it was repeated by us with the remark that the Tyndall experiment is no valid criterion unless precise statements are made as to the size of particles which just appreciably interfere with optical clearness. In other words, the dimensions below which Tyndall's experiment practically fails are here vitally in question, and data for these have not been forthcoming.

Suppose a solid is dropped into an excess of its solvent. In order that the system may become a solution, the disaggregation must at least reach the molecule. In electrolytes it may even go further, as is evidenced by Arrhenius's celebrated factor 2. But under other circumstances may not the separation stop short *before* the molecule is reached; or conversely, when a precipitate is being formed out of individual molecules, may not the process of growth be arrested in virtue of an equilibrium of forces when the particles formed consist of 2, 10, 100, or even 1000 molecules? To answer affirmatively is to find a home for the family of colloidals, and they will more nearly resemble solutions in proportion as the particles are smaller. Certainly the beam of light is no longer an available criterion, for the whole phenomenon is mapped out on a scale which is small even in comparison with the wave-length of light.

2. About a year and a half ago I incidentally made an experiment in connection with certain meteorological questions, which has a precise bearing on the point here at issue. In the endeavour to pass compressed air through a wet porous porcelain septum into water, I was struck by the magnitude of the pressures necessary. Supposing I waited long enough to ensure the transpiration of liquid, no flow of gas through the septum occurred for pressure excesses of even above 100 lbs., excepting at isolated points which were obviously the seat of fissures. Now let T be the surface tension of water in dynes per linear c.m., a the angle of capillarity, r the mean radius of the pores of the septum, and x the pressure of the gas in atmospheres. Then (very nearly)—

$$10^6 x \pi r^2 = 2 \pi r T \cos a,$$

or—

$$r = 2 T \cos a / 10^6 x.$$

If, therefore, in the above experiment $x = 8$ atm., $T = 71$ (Everett's Tables, p. 50), $\cos a = 1$ (say, for the superior limit is in question),

$$r = 18 \times 10^{-6} \text{ c.m.},$$

nearly, making the diameter ($2r$) of the pores smaller than the wave-length of violet light. Schneider showed, however, that colloidal silver passes readily through such a septum, whereas the alcoholic precipitate fails to do so. The particles are therefore respectively smaller and larger than the diameter* given. If 10^{-6} c.m. be taken as the order of molecular dimensions, the size in question is at least 1000 times as large, showing the aggregates to consist of the enormous number of 10^9 molecules at least. There is thus an abundance of room for particles containing (say) 100 molecules to the aggregate, and forming suspensions in water (colloids) in their general aspects hardly distinguishable from true solutions.

It is interesting to ask how great a pressure would force the water out of a septum just large enough to let the particles of the size in question (5×10^{-6} c.m.) pass. It would take several thousand atmospheres, and it is therefore quite impossible to test finer septa like animal membrane to the extent in question. Nevertheless, if the attempt be made to *grade* porous clay septa, prepared by successive vitrifications, by the method given, I dare say that a range of mean diameters of pores could be obtained, sufficient to answer many outstanding dimensional questions† in relation to the colloidal state; but one should be prepared to exert pressures as high as 100 atmospheres.

2. There is another point of view from which colloidal silver invites treatment, this time in the solid state. Dr. Schneider and I interpreted the high degree of insulation which we detected in Carey Lea's metallic mirrors as an instance of the allied behaviour of non-coherent metallic matter in general. Wöhler (quoted by Wernicke) showed this some fifty years ago; but our references were chiefly directed to the recent work of Auerbach (*Wied. Ann.*, xxviii., p. 604, 1886) and of Ed. Branly (*Phil. Mag.*, 5, xxxiv., p. 530, 1892), the latter of whom in particular proved that non-conduction ceased when an electric spark was passed through the column of powder. One therefore readily calls to mind the startling results recently obtained by Oliver Lodge (*Nature*, l., p. 136, 1894) with his "coherer," and the question is pertinently asked whether solid colloidal silver, swept by a train of electric surges, will begin to show increased electric conduction, as it does, for instance, under the influence of heat.

Oberbeck's (*Wied. Ann.*, xlvi., p. 265, 1892; xlvii., p. 353, 1892) electric work, undertaken in a different direction with a view of showing the occurrence of an allotropic state in Carey Lea's silver, has quite failed to convince us. We see no reason for withdrawing the views which we originally expressed (*loc. cit.*).

3. At the close of our experiments (Barus u. Schneider, *Wied. Ann.*, xlviii., p. 336, 1893) we suggested that a field of great promise would be found in the metallic optics of colloidal silver. Work of this kind has since been taken up with success by Wernicke (*Wied. Ann.*, li., p. 448, 1894; lii., p. 515, 1894). The change of phase observed on the reflection of light from thin metallic laminæ enclosed between clear media, with the front plate of greater refractive index, is either an acceleration or a retardation, according as the metal is intrinsically coherent or non-coherent. The method is remarkably sensitive and applicable to metallic films so thin as to be quite invisible to the eye. Tested in this way colloidal silver according to Wernicke (*loc. cit.*, p. 523) takes rank with bodies which in their ultimate nature are an aggregate of individual particles, however small they may be, or however perfect the mirroring surface which an even distribution may produce. It is this method which is to be looked to for decisive results, not only for silver, but for other colloids.

4. Of the two interpretations which may be given of Carey Lea's brilliant discovery, the one originally advocated by Dr. Schneider and myself is to me intensely the

* By the hydrodynamic method particles smaller than 2×10^{-6} were measured, supposing the method vouched for.—*Ostwald's Zeitschrift, loc. cit.*

† I may here call to mind the allied geological fact that hot water will pass through porous rock in virtue of capillarity, in the face of enormous withstanding steam pressures.

more interesting. As an aggregate of excessively fine suspended particles, colloidal silver introduces a whole series of fascinating physical problems, subject to forces which as to their nature are almost tangible. Even in an ordinary case of sedimentation if I write—

Muddy water + acid = acidulated water + mud,

the latter body being precipitated, I have a chemical equation in embryo,—an equation* which so far as can now be discerned lacks stöchiometric precision, but which in its general character is undoubtedly a double decomposition. If the actuating forces be traced, they must lead by slow gradations up to affinity.—*American Journal of Science*, xlviii., December, 1894.

THE DETERMINATION OF PHOSPHORIC ACID BY THE MOLYBDATE-MAGNESIA METHOD.

By B. W. KILGORE.

For the investigation of the official molybdate method as used by the American Association of Official Agricultural Chemists for 1894, three samples were sent to various agricultural and commercial chemists with instructions for analysis.

No. 1 was a mixture of cotton-seed meal and castor pomace, containing about 2½ per cent P_2O_5.

No. 2 was an acid phosphate with about 17 per cent P_2O_5.

No. 3 was a phosphate solution containing 10 grms. C. P. disodium hydrogen phosphate ($Na_2HPO_4+12H_2O$) to the litre, the theoretical percentage of P_2O_5 in this salt being 19·826.

The discussion, which will be made here, of this work will be confined to the results obtained on solution No. 3, as it was the only sample whose content of P_2O_5 was definitely known. Twenty-eight chemists reported thirty-four determinations on No. 3, the highest of which was 20·67 per cent, and the lowest 19·74 per cent, the latter being 0·086 of 1 per cent below the theory, and the former 0·844 per cent above. The average of all results was 20·09 per cent, or 0·264 of 1 per cent above the theory; the variation between highest and lowest results was 0·93 of 1 per cent; the variation below the theory was 0·086, and above the theory 0·844 of 1 per cent. Eighteen per cent of the determinations were within 0·05 of 1 per cent of the theory, 36 per cent within one-tenth, and 44 per cent within two-tenths. In the work on this sample a few analysts have gotten results reasonably close to the theory, a great many have varied widely from it, and nearly all have gotten high results, which brings me to the point to which I desire to draw especial attention, and that is the tendency of the molybdate-magnesia method to give high results, even when the greatest care is exercised, as is reasonable to suppose was the case in this test work. I might add here that nearly all the chemists taking part in this work had had some years experience with the method, and those who had not worked under good supervision.

The tendency of the method then, it seems, is for high results, and it is in order to ask where the trouble lies.

The phosphate solution sent out was precipitated directly with magnesia mixture by four chemists, when they obtained (1) 19·92, (2) 19·93 and 19·94, (3) 19·91 and 19·85, and (4) 20·03 and 20·05 per cent P_2O_5, against (1) 19·93 and 19·87, (2) 19·93 and 19·91, and (3) 19·93 and 20·06 by precipitating with molybdic solution first.

The results here by both methods of procedure, while slightly high most of them, are practically the same whether precipitation was made direct with magnesia mixture, or previously with molybdic solution. This argues that the trouble is not in the molybdate precipitate or precipitation. The magnesium ammonium phosphate precipitate obtained from this sample in the usual way was, after washing, dissolved by one chemist in hydrochloric acid and re-precipitated with ammonia, when he obtained 19·80 and 19·81 per cent P_2O_5, while another added 1 grm. citric acid to the alkaline solution in which the "white precipitate" is formed, and obtained 19·83 and 19·83 per cent P_2O_5 against 20·06 and 19·93 by the regular method.

The results by the last two methods of procedure are, while few, close to the theory, and indicate that in the regular molybdate-magnesia method that either some of the magnesium of the magnesia mixture is thrown down as hydroxide and contaminates the precipitate, or else the magnesium ammonium phosphate formed under the conditions of precipitation contains more than a normal amount of magnesium, and that by dissolving the "white precipitate" in hydrochloric acid and re-precipitating, and also by the presence of citric acid in the solution where the "white precipitate" is formed, the trouble is prevented.

H. Neubauer (Abstract *Journal Chemical Society*, October, 1893, 489) has shown that magnesium ammonium phosphate formed in solutions containing an excess of both ammonia and magnesium salt, which is the condition of precipitation in the method under discussion, contains more than a normal amount of magnesium. The writer has had magnesium of the magnesia mixture to deposit as hydroxide and contaminate precipitates where very large excesses of the magnesia mixture were used in strongly alkaline solution and on long standing, though little or no error is thought to be introduced by this latter cause where the prescribed amount of magnesia mixture is used and too long standing not allowed. It is to the excess of magnesium in the magnesium ammonium phosphate, we consider, that the high results by the molybdate-magnesia method are due.

The results upon which the foregoing discussion is based will appear in the proceedings of the A. O. A. C. in the "Report on Phosphoric Acid," made by the writer to that association at its recent meeting.—*Journal of the American Chemical Society*, xvi, No. 12, December, 1894.

* In the same way I picture to myself the remarkable physical effects produced by traces of foreign admixtures in metallurgy.

NOTICES OF BOOKS.

Elementary Nature of Chlorine. Papers by Humphry Davy. (1809—1818). Edinburgh: W. F. Clay. London: Simpkin, Marshall, and Co., Limited. Crown 8vo., pp. 80.

This collection of papers is No. 9 of the "Alembic Club Reprints," which we have had the pleasure of noticing.

For a due appreciation of Davy's papers and of the "Chlorine Controversy" altogether, we must remind the reader that in the beginning of the century chlorine was regarded as an oxygen-compound of muriatic acid, which latter substance was doubtfully held to be simple. There are doubtless persons yet living who can remember that in the days of the excise duty upon common salt every bleacher or other person using chlorine in his business was obliged to have affixed to his establishment a sign-board bearing the inscription, "Licensed manufacturer of oxygenated muriatic acid." Of course this sign was — characteristically enough — still required after the elementary character of chlorine was proved and recognised.

In the papers before us Davy had firstly to show that muriatic acid gas was a compound of a body still unknown

in a separate state, as was held by Gay-Lussac and Thénard. He next investigated chlorine which had been discovered by Scheele and pronounced to be muriatic acid free from hydrogen, or in the language of his time "dephlogisticated muriatic acid." Gay-Lussac and Thénard suggested that it might be a simple substance, but Berthollet concluded that it was a compound of muriatic acid gas and oxygen, a view which prevailed for nearly twenty years, and which was only refuted by Davy in the present papers. It will be seen that he did not set out with any *à priori* idea of the elementary character of chlorine, but was guided by experiment. He traces certain analogies between chlorine and oxygen, and proposes for the former the name chlorine, which was soon generally accepted. In the last of the papers here reproduced, bearing date February 12th, 1818, he shows the fallacy of the experiments in which chlorine was said to have been decomposed with a formation of water.

With true philosophic caution Davy declines to pronounce either oxygen, chlorine, or fluorine to be elements, but simply asserts that they have not yet been decomposed.

Photomicrography. By Dr. Henry van Heurck. English Edition. Re-edited and Augmented by the Author from the Fourth French Edition, and Translated by W. E. Baxter, F.R.M.S., F.G.S. London: Crosby Lockwood and Sons. 1894.

This pamphlet is extracted from Dr. Van Heurck's exhaustive treatise on "The Microscope: Its Construction and Management," and is now, with the author's sanction, first published in a separate form.

All that the eye can see through the microscope, and even more, can be reproduced by the sensitised plate; from the time of the first discovery of photography, many workers were experimenting on the best means of obtaining good results as early as 1844. Douné and Léon Foucault published their "*Atlas d'Anatomie Microscopique*," which was compiled from daguerreotyes, and the first paper proofs are believed to have been produced by Bertsch about the year 1857. Since that time many others have been engaged on the subject, and the results which are now obtained are wonderful evidence of the great mechanical and manipulative skill which has been obtained.

The author here gives full descriptions of the several forms of apparatus now in vogue, the letterpress being augmented by a number of excellent illustrations; all details of manipulation and procedure are gone fully into, and we feel that we may safely congratulate the author on having produced an excellent and trustworthy book. The value of photography in modern science is daily becoming of more and more importance, and this special branch of the subject is likely to be one of the most useful in preserving records of minute observations, which are not effected by the "personal equation" of the observer.

The Dynamics of Life. An Address delivered before the Medical Society of Manchester, October 3, 1894. By W. R. Gowers, M.D., F.R.S. London: J. and A. Churchill. Small 8vo., pp. 70.

The author of this address, after having spoken ably and thoughtfully of the dynamics of muscle and the dynamics of nerve, makes a noteworthy admission: "I have spoken," says he, "of the dynamical processes which occur under the influence of life, but nothing about the dynamics of life itself. If you anticipate that I shall come to this, I cannot but disappoint you. Of the relation of energy to life itself there is, it seems to me, nothing to be said. Not only is the relation of energy to vitality entirely hidden from us now, but I can see no promise that the future has it in store for us." In this address we find abundant proof, if such were needed, of the imperfection of our biology.

Still, the author, if he has added little or anything to our knowledge of life, is doing good service in sweeping away misconceptions. But research—research without limit—is wanted, and this cannot be afforded! Organised ignorance is allowed to threaten the inquirer with fine and imprisonment, and the most highly qualified physician is deprived by the so-called "battle of life" of the leisure necessary for even attempting to arrive at new truth.

The distinguishing name which Dr. Gowers proposes to apply to the motions of visible bodies in contradistinction to that of atoms and of molecules, *i.e.*, "massive," seems to us less satisfactory than "molar" as commonly used. We may also think it injudicious of the author to select sound as an *atomic* vibration. On the other hand, he does well to point out the error of calling the longitudinal shortening of muscular fibres "contraction."

The following reflection is very salutary:—"We cannot help seeing that which we cannot see through. Some of our most stubbon facts permit no light to reveal even the outline of that which is within them." Not less philosophical is the remark that "between what we term 'theory' and 'fact' the transition is very gradual; that much of that which we regard as fact is only fact to our thought."

Dr. Gowers, in his address, was speaking to medical practitioners, perhaps also to medical students. But it may be profitably read also by non-medical biologists.

On Line Spectra (*Wied. Annalen* and *Zeitschrift Physik. Chem.*).—J. R. Rydberg has undertaken a full discussion of the spectra of calcium and strontium with the view of establishing in a definite manner the relations among the spectra of analogous elements. He points out that the reasons are increasing which support in any element the admission of a single system of vibrations and the prospect of including all the lines of a spectrum in a single formula, in opposition to the view of a mixture of spectra belonging to molecules of various temperatures. It seems very probable that each element has only a single spectrum. The author's views are supported by H. Kayser and C. Runge (*Wied. Annalen*).

Experimental Researches made on the Crystallisation-point of certain Organic Substances.—Raoul Pictet (in conjunction with Dr. Baron von Schneider and Dr. Altschul).—The organic substances have been first carefully purified. The authors purposely selected substances one radicle of which is the same in several successive bodies, so as to distinguish the effect of *introduction* in a definite group of a mol. of CH_3, or of the *substitution* of chlorine for hydrogen. They are able to recognise a general law on the influence of the introduction in any group of the aromatic series of a mol. CH_3; this mol. always *lowers* the point of congelation. We see, for instance, benzene, C_6H_6, congeal at $+4°$. If we introduce a mol. of methyl, CH_3, we obtain toluene, which does not crystallise even at $-100°$. If we substitute a Cl for a H of the methyl group which enters into a radicle, the congelation-point is raised. If we substitute 3Cl for the 3H atoms of H, this elevation of the congelation-point stops. We have been able to verify in a series of experiments the exactitude of Bäyer's law. He has observed that, in homologous substances having a structure comparable as regards the position of the carbon, the congelation-points rise or descend according as the number of atoms of C is even or odd. Substances possessing an odd number of C crystallise at the lowest temperatures. The more the mol. of a substance as compared with a substance adjoining it in the series exhibits symmetry in its constituent atoms, the more it is compact, homogeneous, with a symmetrical grouping of its elementary, radicles the more readily its congelation is effected at a temperature comparatively high.—*Comptes Rendus*, cxix., No. 23.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Zeitschrift für Anorganische Chemie, Vol. vii., Part 3.

Reduction of Arsenic Acid by the Action of Hydrochloric Acid on Potassium Bromide.—F. A. Gooch and I. K. Phelps.

Detection and Approximate Determination of Small Proportions of Arsenic in Copper.—F. A. Gooch and H. P. Moseley.—Already inserted.

Iodometric Determination of Telluric Acid.—F. A. Gooch and J. Howland.—Already inserted.

Action of Ferric Sulphate upon Potassium Iodide and Hydriodic Acid.—Karl Seubert and R. Rohrer.—This paper would require to be accompanied by several diagrams of curves and extensive tables.

Analysis of Apatite from the Large-Leaved Graphite of Ceylon.—Paul Jannasch and J. Locke.—The composition of the mineral was $Ca_5P_3(F.Cl.OH)O_{12}$. The specimen had an oily green colour, and was surrounded by a brown dull substance. The hardness was that of apatite.

Reduction of Vanadic Acid by the Action of Tartaric Acid and its Titration with Iodine in an Alkaline Solution.—P. E. Browning.—Inserted in full.

Electrolysis of Nitrosyl Sulphuric Acid in a Sulphuric Solution.—A. Gurchman.—This paper requires the accompanying cut.

Researches on the Volatility of Mercuric Chloride.—H. Arctowski.—The three accompanying figures are here requisite.

On the Sulphuromolybdates.—Arthur Rosenheim.—The author having previously studied the well-characterised compounds of the oxalates with the vanadates observed analogous compounds among the sulphuromolybdates. The author describes the ammonium salt, and those of potassium and sodium.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. ix., No. 105.

Report presented by Aime Girard, on behalf of the Committee of Chemical Arts, concerning a New Apparatus for Concentrating Sulphuric Acid, invented by Kessler, of Clermont Ferrand.—The report shows that the stills for concentrating sulphuric acid, whether of glass, of platinum, or platinum boilers, require to be fitted with a dome of lead. Of late a stronger kind of sulphuric acid has come into demand, containing, not as formerly from 92 to 93 per cent of monohydrated acid, but from 96 to 98, or even 99 per cent. The concentration is thus rendered more difficult. If we work in glass the retorts are apt to be broken by "bumping," and platinum is dissolved in a proportion which becomes higher the more concentrated the acid. For acid at 99·5 per cent the loss per ton is 9 grms., which at the present price of 16 francs per kilo. amounts to 1·44 francs per 100 kilos. of concentrated acid. M. Kessler instead of applying the heat to the bottom or the sides of the retorts causes hot gases from an adjoining furnace to act upon the surface of the acid. The gases are at once saturated with watery vapour, and the acid when it has reached its maximum concentration is run off at the surface. The apparatus, which is shown in the figures, is constructed of the lava of Volvic, of natural grit-stone or of ceramic grits. The apparatus yields easily in 24 hours 5000 kilos. of acid containing 96 to 98 per cent of the monohydrated acid. The cost of the plant is only 3000 francs, whilst a platinum apparatus yielding an equal quantity of acid costs 30,000 francs. The consumption of fuel is reduced one-half, the waste of metal is abolished, and the acid is free from all nitrous compounds. The apparatus is found, we learn, to be giving full satisfaction at the various works where it has been introduced.

MISCELLANEOUS.

Appointment.—The appointment as Director of the State Physico-Technical Institute in Berlin, in succession to the late Professor von Helmholtz, has been offered to, and accepted by, the well-known Dr. Kohlrausch, Professor of Physics at Strassburg University.

MEETINGS FOR THE WEEK.

Tuesday, Jan. 1st.—Royal Institution, 3. "The Working of an Electrical Current," by Prof. J. A. Fleming, F.R.S.
—— Pathological, 8.30.
Thursday, 3rd.—Royal Institution, 3. "The Working of an Electric Current," by Prof. J. A. Fleming, F.R.S.
Friday, 4th.—Quekett Club, 8.
—— Geologists' Association, 8.
Saturday, 5th.—Royal Institution, 3. "The Working of an Electric Current," by Prof. J. A. Fleming, F.R.S.

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THE MINERAL INDUSTRY: Its Statistics, Technology, and Trade, in the United States and other Countries, from the Earliest Times, being the Annual Statistical Supplement of the *Engineering and Mining Journal.* Edited by RICHARD P. ROTHWELL. Price, Vol. I. for year 1892, 12s. 6d.; Vol. II. for year 1893, 25s.

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